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A microprocessor-controlled ion selective electrode (MC) method was evaluated and compared to the forward amperometric titration (AT) method for determining total chlorine in condenser cooling river water from coal-burning electric plants. The effective range for quantification by the MC method is from the minimum detection limit of 6.5 μg/l chlorine for unspiked condenser water and 13.3 μg/l chlorine for spiked condenser water to 100 μg/l chlorine. Interferences by zinc(II), copper(II), iron(III), arsenic(III), and manganese(VII) are discussed. The pH, chromium(VI), mercury(II), bromide, and arsenic(V) do not interfere with measurement of total chlorine. For both unspiked and spiked condenser water, the overall pooled standard deviation and overall mean percentage relative standard deviation over concentrations of 20-200 μg/l chlorine are lower for the MC method than for the AT method. Standard deviations are discussed for the MC method over concentrations of 2-20 μg/l chlorine.

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by

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ABSTRACT

A microprocessor-controlled ion selective electrode (MC) method was evaluated and compared to the forward amperometric titration (AT) method for determining total chlorine in condenser cooling river from coal-burning electric plants. The effective range for quantification by the MC method is from the minimum detection limit (MNDL) of 6.5 μg/l chlorine for unspiked condenser water and 13.3 μg/l chlorine for spiked condenser water to 100 μg/l chlorine. Interferences by zinc(II), copper(II), iron(III), arsenic(III), and manganese(VII) are discussed. The pH, chromium(VI), mercury(II), bromide, and arsenic(V) do not interfere with measurement of total chlorine. For both unspiked and spiked condenser water, the overall pooled standard deviation and overall mean percentage relative standard deviation for concentrations from 20 to 200 μg/l chlorine are lower for the MC method than the AT method. Standard deviations are discussed for the MC method for concentrations from 2 to 20 μg/l chlorine.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ASTM --American Society for Testing and Materials

AT --forward amperometric titration method

°C --degrees Celsius (centigrade), equals degrees Kelvin minus 273

EMSL --Environmental Monitoring and Support Laboratory

EPA --U.S. Environmental Protection Agency

FAS --ferrous ammonium sulfate

g --gram

h --hour

l --liter, equals 0.001 m^3

LCL --lower 95% confidence limit

m --meter

m- --milli-, $x10^{-3}$ (as a prefix, e.g., mm)

M --molar, mole per liter

MC --microprocessor-controlled ion selective electrode

min --minute

MNDL --minimum detection limit

N --normal, equivalent per liter

NBS --National Bureau of Standards

PAO --phenylarsine oxide

RSD --relative standard deviation

LIST OF ABBREVIATIONS AND SYMBOLS
(Continued)

s --second

SD --standard deviation

t --student t statistic

TVA --Tennessee Valley Authority

UCL --upper 95% confidence limit

SYMBOLS

$\overset{-}{e}$ --electron with negative charge of one

μ- --micro-, x10^{-6} (as a prefix, e.g., μm)

% --percent

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SECTION 1

INTRODUCTION

Because numerous studies have documented the toxicity of low levels of chlorine and its byproducts for aquatic organisms and because current technology makes it possible to reduce substantially the amount of chlorine used to control biological organisms that foul once-through cooling water systems, the U.S. Environmental Protection Agency (EPA) recently proposed that total chlorine discharges to surface waters be limited to 0.14 mg/l (1). A precise and accurate method of measuring very low concentrations of total chlorine is needed both for routine monitoring of cooling-tower operations and for assessing compliance with this proposed discharge limit.

Among the methods now recommended by EPA for monitoring total chlorine in all types of waters and wastes that do not contain appreciable quantities of organic matter is the forward amperometric titration (AT) method (2), which is identical to the ASTM D1253-76-A direct amperometric titration method (3). In recent collaborative tests, however, the average operator precision (standard deviation) of the AT method was about 0.03 mg/l total chlorine (4,5). At concentrations of about 0.02 mg/l total chlorine, determinations were hampered by lack of highly precise conditions for the equipment used in the analysis (5).

One promising alternative to the AT method is the microprocessor-controlled ion selective electrode (MC) method. During development of this method (6,7), experimental determination of total chlorine in "spiked" standards with combined chlorine (deionized water with known additions of chlorine using chloramine T), public water supply samples, and swimming pool water samples indicated the minimum detection limit of the MC method to be about 0.002 mg/l (values of 0.003 and 0.004 mg/l were actually reported), at least for these applications. These studies also indicated that 0.1 mg/l was the highest concentration that could practically be determined. These earlier experiments did not test the MC method with "spiked" standards of calcium hypochlorite [a free chlorine source used as a biocide (8)], compare the results of the AT and MC methods, or test the MC method for determining total chlorine in untreated river water or chlorinated river water used for condenser cooling, which could contain other chemicals that might interfere with the accuracy and precision of measurements or degrade the detection limit.

However, if the MC method could provide the same quality of results for samples of river water and cooling water, the 10-fold improvement in sensitivity [compared to the estimated minimum detection limit of 0.02 mg/l for the AT method that can be calculated from minimum amount (0.02 ml) of 0.00564-N phenylarsineoxide (PAO) titrant dispensed when titrating a 200 ml sample by the standard method (2-4,9)] would make it a useful method for monitoring cooling water treated with the minimum levels of chlorine (needed to produce enough free chlorine to control biofouling) and for assessing compliance with the proposed limit for chlorine discharges to surface waters.

The MC method indicates chlorine concentrations by measuring the iodine that results from the complete reaction of chlorine with an excess of potassium iodide in an acetate buffer at pH 4.0 (the same chemistry used for the AT method). The Orion Research Model 97-70 total chlorine electrode used for the MC method (10), contains a platinum element that develops an electromotive force (potential) in proportion to the iodine that is produced (the potential developed depends on relative levels of iodine and iodide in solution) and an iodide-sensing element that develops a similar potential in proportion to the excess iodide that remains in solution following the reaction. By measuring the difference between these potentials, the MC method determines the iodine concentration, which (because the reaction proceeds to completion) equals the original concentration of chlorine. This electrode used without a microprocessor, has a useful range up to 20 mg/l.

After the reagents have been added to the sample, the microprocessor automatically

(a) controls a buret to make a series of additions of known, minute volumes of a standard chlorine solution (the number of additions is determined by the operator),

(b) computes the Gran function (G_i) for each electromotive force value sensed by the ion selective electrode after each volume addition (i) of the standard chlorine solution,

(c) estimates (by algebraic solutions of the slope and intercept values for least-squares analyses of the G_i and i values) the most nearly linear fit for a subset of 35 volume additions and calculates from this a total chlorine concentration for that subset,

(d) drops the first five data points of the first subset and adds five new data points to form a second subset,

(e) determines the difference between the chlorine concentration values calculated for that pair of subsets,

(f) continues in this manner until all volume additions have been analyzed in overlapping subsets and the differences between concentrations for each pair of subsets have been determined,

(g) determines which pair of subsets has the least difference between the total chlorine concentrations calculated for its first and second subsets, and

(h) displays the value calculated for the first subset of the selected pair as the best indication of the total chlorine concentration of the sample (6,7,11,12).

Because the microprocessor combined with the Orion 97-70 electrode lowers the minimum detection limit from 0.01 to 0.002 mg/l chlorine and reduces the maximum detection limit from 20 to 0.1 mg/l, the effective range for quantification by the MC method is 0.002 to 0.1 mg/l (6,7,10). The addition of a small amount of sodium hydroxide to the potassium iodide reagent for the MC method eliminates need for a blank to obtain a linear curve for low concentrations (6,10).

Chemical contaminants present in a sample could interfere with chlorine determinations by the MC method. These include (a) those that alter the pH of the solution; (b) those that oxidize potassium iodide at pH 4.0, just as total chlorine does, and produce an extraneous source of iodine (2,3,10); (c) those that inhibit or poison the sensitivity of the platinum iodine-sensing element of the electrode or otherwise affect its operation (10); and (d) those that complex with iodine, which is predominantly present as tri-iodide, I_3^-, in solutions containing excess iodide (13), to form chelated compounds that either cannot be sensed by the platinum element or that alter the potential it develops. River water and condenser cooling water (14) may contain oxidizing chemicals such as chromium(VI), iron(III), and manganese(VII); platinum-sensing poisons such as mercury(II) and arsenic(III); or chelating chemicals such as zinc(II) and copper(II).

Although the same iodimetric chemistry at pH 4.0 is used for both the MC and AT methods, there is little information available from investigations of the AT method that can be used to assess the effects of chemical interference on the MC method. Manabe (15) found that the interference with the AT method caused by iron(III) and copper(II) could be eliminated by pyrophosphate.

The purpose of this work, therefore, was to assess the accuracy, precision, and detection limit of the microprocessor-controlled ion selective electrode (MC) method for use in routine measurements of microgram-per-liter concentrations of total chlorine in the chlorinated river water used for condenser cooling at coal-burning electric power plants. The research included comparative laboratory and field tests of the MC and AT methods for determining total chlorine concentrations in both simulated and actual samples of cooling water and tests of the interference caused by chemicals typically found in river water and cooling water.

The laboratory tests evaluated

(a) the maximum detection limit (the highest concentration of total chlorine that could practically be determined by the MC method); the effects of interference by pH, chromium(VI), mercury(II), bromide, zinc(II), copper(II), iron(III), arsenic(III), and manganese(VII); and the effects of pyrophosphate in overcoming interference by zinc(II), copper(II), and iron(III) in deionized water spiked by adding accurately known quantities of chlorine from standard solutions of chloramine-T or calcium hypochlorite;

(b) the precision, accuracy, and minimum detection limit (the lowest concentration that could practically be determined by the MC method) for determining total chlorine in deionized water and river water spiked by adding accurately known quantities of chlorine from standard solutions of chloramine-T, calcium hypochlorite, or both; and

(c) the comparative precisions, accuracies, and minimum detection limits of the MC and AT methods for determining total chlorine in deionized water and river water spiked by adding accurately known quantities of chlorine from standard solutions of chloramine-T, calcium hypochlorite, or both.

The field tests compared the precisions, accuracies, and minimum detection limits of the MC and AT methods for determining total chlorine concentrations in

(a) samples of chlorinated condenser cooling water collected at four TVA coal-burning electric power plants, and

(b) samples of chlorinated condenser cooling water collected at four TVA coal-burning power plants and spiked by adding accurately known quantities of chlorine from standard solutions of calcium hypochlorite.

SECTION 2

CONCLUSIONS

A microprocessor-controlled ion selective electrode (MC) method has been evaluated and compared to the forward amperometric titration (AT) method for determining total chlorine in spiked and unspiked condenser cooling river water.

The highest concentration of total chlorine that can be practically determined with suitable precision and accuracy by the MC method is 100 μg/l chlorine. The pH in the 3.6-4.4 range, chromium(VI) at 500 μg/l, mercury(II) at 10 μg/l, and bromide at 100 μg/l do not affect recovery of total chlorine. A concentration of 990 μg/l of zinc(II), 500 μg/l of copper(II), and 5 mg/l of iron(III) do not appreciably affect recovery of total chlorine. However, a concentration of 10 mg/l of zinc(II), 5 mg/l of copper(II), and 9.9 mg/l of iron(III) do interfere. Concentrations of 500, 200, and 50 μg/l of arsenic(III) interfere, whereas concentrations of 200 and 50 μg/l of arsenic(V) do not. A concentration of 990 μg/l of manganese(VII) also interferes.

For the MC method, for concentrations from 2 to 20 μg /l chlorine in unspiked, chlorinated condenser water, the total chlorine overall pooled standard deviation is 2.1 μg/l and the overall mean percentage relative standard deviation is 20.8. For concentrations from 20 to 200 μg /l chlorine in unspiked, chlorinated condenser water, the total chlorine overall pooled standard deviation of 6.3 μg/l and overall mean percentage relative standard deviation of 7.7 by the MC method is lower than the total chlorine overall standard deviation of 8.7 μg/l and overall mean percentage relative standard deviation of 12.9 by the AT method. The overall, pooled minimum detection limit (MNDL) of 6.5 μg /l chlorine by the MC method in unspiked condenser water is lower than that of 17.8 μg /l chlorine by the AT method.

The Student t value -0.091 with mean difference of -0.1 μg /l chlorine and standard deviation of 13.0 μg /l chlorine for 112 split samples of unspiked, chlorinated condenser water analyzed for total chlorine by the MC and AT methods for concentrations from 20 to 200 μg /l chlorine shows there is no reason to conclude the mean of the differences between the MC and AT methods differs from zero at 95 percent significance.

For the MC method, for concentrations from 2 to 20 μg /l chlorine, the total chlorine overall standard deviations of 1.9 and 2.1 μg/l are similar for spiked and unspiked condenser water. For concentrations from

20 to 200 µg/l chlorine in spiked, chlorinated condenser cooling river water, the total chlorine overall pooled standard deviation of 8.7 µg/l and the overall mean percentage relative standard deviation of 10.4 by the MC method is lower than the total chlorine overall pooled standard deviation of 10.2 µg/l and overall mean percentage relative standard deviation of 19.6 by the AT method. For spiked condenser water, the overall MNDL of 13.3 µg /l chlorine by the MC method is lower than that of 22.2 µg/l chlorine by the AT method.

SECTION 3

RECOMMENDATIONS

The microprocessor-controlled ion selective electrode (MC) method described in this report has equivalent or better sensitivity, precision, and accuracy than the forward amperometric titration (AT) method for determining total chlorine in condenser cooling river water at coal-burning electric power plants. Therefore, the authors recommend its use for determining chlorine at concentrations from 7 to 100 μg/l in chlorinated condenser cooling river water. Higher concentrations of chlorine can be determined by dilution.

In its present state of development, the MC method has three main limitations which would impair the practical use of this instrument:

a. the size of equipment and power requirements restrict the mobility required in power plant chlorine monitoring;

b. the time required to assay a sample (3-4 minutes typically) restricts the number of sample analyses possible during the chlorination periods (typically 20-30 minutes);

c. free chlorine, not total chlorine, is the main factor to maintain condenser efficiency.

Because of these limitations, the amperometric titration (AT) method is sufficient in both ease of use and sensitivity to meet power plant needs; however, the MC method could be utilized in special studies of a nonroutine nature for which the AT method is not suited.

SECTION 4

EXPERIMENTAL

SAMPLE PREPARATION

Synthetic Samples

For tests of the precision and accuracy of the MC and AT methods, aliquots of deionized water, river water, and chlorinated river water used for condenser cooling at the coal-burning electric power plants tested were spiked by chlorinating sequential portions with accurately known quantities of chlorine from standard solutions of chloramine-T, calcium hypochlorite, or both to yield the expected concentrations shown in Tables 1-4.

For tests of chemical interference with the MC method, deionized water aliquots were spiked individually with chromium(VI), mercury(II), bromide, zinc(II), copper(II), iron(III), arsenic(III), arsenic(V), and manganese(VII) to give the final concentrations shown in Table 5. The 10-mg/l concentration of zinc(II), the 5- and 500-mg/l concentrations of copper(II), and the 5-mg/l concentration of iron(III) for the interference studies were prepared by diluting the 1000-mg/l standard solution of the respective element with deionized water, while the 1000-mg/l concentrations of zinc(II) and iron(III) were drawn from the 1000-mg/l standard solution of the respective element. The 2 percent (w/v) solution of sodium pyrophosphate decahydate salt for overcoming interference by copper(II), iron (III), and zinc(II) was prepared by dosing a 50-ml aliquot of test solution with 1 g of the salt dispensed by adding 2 scoops from a calibrated measuring spoon (Catalogue Number 907, Hach Chemical Company, Ames, Iowa).

The pH 3.6, 3.8, 4.0, 4.2, and 4.4 buffer solutions for the interference tests were prepared by dispensing 10 ml of deionized water and 55.9 ml of glacial acetic acid in a series of five 150-ml pyrex beakers, slowly adding 10-M sodium hydroxide, mixing the contents to adjust solutions sequentially in the beakers to pH values of 3.6, 3.8, 4.0, 4.2, and 4.4, and diluting each solution to 100 ml. The 10 M sodium hydroxide used for adjusting the pH was prepared by dissolving sodium hydroxide pellets in deionized water and diluting the solution to 1000 ml (CAUTION! Wear gloves and safety goggles. Sodium hydroxide attacks the skin and blinds).

The synthetic samples of mercury(II), zinc(II), and copper(II) were drawn from 1000-mg/l certified atomic emission standard solutions (Spex Industries Incorporated, Metuchen, New Jersey) and diluted with deionized water to form tne respective 50-, 100-, and 50-mg/l stock spiking solutions shown in Table 5. The 50-mg/l concentration of chromium(VI) shown in Table 5 was prepared gravimetrically from potassium dichromate (0.1414 g in 1000 ml of deionized water); weights were checked against reference weights traceable to the National Bureau of Standards (NBS). The 50-mg/l concentration of bromide was prepared by dissolving exactly 0.0745 g of potassium bromide (previously dried for 6 h at 150°C) in deionized water and diluting the solution to 1000 ml in a volumetric flask. The 1000-mg/l concentration of iron(III) was prepared by dissolving 8.634 g of ferric ammonium sulfate dodecahydrate in deionized water and diluting the solution to 1000 ml in a volumetric flask.

The 50-mg/l concentration of arsenic(III) stock spiking solution shown in Table 5 was prepared by diluting the 1000-mg/l concentration of arsenic(III). The latter concentration was prepared by weighing 4.0 g of sodium hydroxide pellets in a 150-ml pyrex beaker (CAUTION! Wear safety goggles. Sodium hydroxide attacks the skin and blinds), weighing 1.320 g of arsenic(III) oxide in a metal pan, and quantitatively transferring the arsenic(III) oxide to the beaker with about 25 ml of deionized water. When the solid had dissolved completely with the aid of stirring, the solution was transferred quantitatively to a one-liter volumetric flask containing a few hundred milliliters of deionized water and diluted to 1000 ml. The 50-mg/l and 1000-g/l concentrations of arsenic(V) were prepared similarly except that 1.534 g of arsenic(V) oxide were used.

The 100-mg/l concentration of manganese(VII) stock spiking solution shown in Table 5 was prepared by diluting potassium permanganate that had been standardized against sodium oxalate (16). Because the equivalent weight of manganese(VII) is 10.99, the normality (0.0525) of standard permanganate multiplied by 10990 gives the concentration of manganese(VII) in the stock solution (577 mg/l) that was diluted to yield the stock spiking solution shown in Table 5.

EQUIPMENT

Total chlorine was measured by the MC method (6,7) with equipment designed and fabricated by Lawrence Livermore Laboratory, Livermore, California (17) and by the forward amperometric titration method (2) with a Model 17T1010 amperometric titrator obtained from Fisher and Porter Company, Warminster, Pennsylvania (9).

PREPARATION OF SOLUTIONS FOR CONDUCTING TESTS

Reagent-grade chemicals were used to prepare all solutions.

The titer of the 0.0375-N phenylarsine oxide (PAO) reagent (Hach Chemical Company, Ames, Iowa) was determined by standardization against 0.05000-N potassium biiodate, while that of the 0.00564-N PAO (Fisher and

Porter Company, Warminster, Pennsylvania) was verified against 0.00500-N potassium biiodate (2). Also the strength of the 0.001128-N PAO, which was prepared by diluting the 0.00564-N PAO, was checked against 0.00500-N potassium biiodate (2). Results found agreed with those certified.

The 0.0282-N ferrous ammonium sulfate (FAS) reagent was prepared by dissolving 11.06 g of ferrous ammonium sulfate hexahydrate in deionized water containing 1 ml of a mixture of one volume of sulfuric acid in three volumes of water (CAUTION! Wear gloves and goggles. Sulfuric acid causes severe burns. It must be added to water slowly. Heat is evolved during this addition), diluting the solution to 1000 ml, and standardizing it against 0.0705-N potassium dichromate that had been prepared by dissolving 3.4567 g in 1000 ml of deionized water (16). Results found agreed with those expected.

The standard 0.0375-N PAO and 0.0282-N FAS reagents were used to assay for total chlorine (2,16) in the 2000-mg/l chlorine solutions of chloramine-T and calcium hypochlorite to establish the true concentration of chlorine. Assay results for titration with 0.0282-N FAS were 5 to 15 percent lower than those for titration with 0.0375-N PAO. Because the end point in the FAS titration (16) was obscured by turbidity, the assay with FAS was abandoned in favor of assay with PAO (2).

The 2000-mg/l solution of chloramine-T as chlorine was prepared by dissolving 7.945 g of sodium N-chloro-p-toluenesulfonamide trihydate (chloramine-T trihydrate, Catalogue Number 6-E494, J. T. Baker Chemical Company, Phillipsburg, New Jersey), which has an equivalent weight of 140.8, equal to one-half of its molecular weight of 281.69 as shown by half-reaction in equation 1, in deionized water and diluting the solution to 1000 ml in a volumetric flask:

$$CH_3C_6H_4SO_2NCl^- + H^+ + 2\ e^- \rightarrow Cl^- + CH_3C_6H_4SO_2NH^-. \qquad (1)$$

This solution was stored in a borosilicate glass bottle that had been sealed with a cone-shaped polyethylene-lined screw-cap and wrapped in aluminum foil to protect from decomposition by sunlight. Assay results with 0.0375-N PAO (2) verified that this solution contained 2000 mg/l of total chlorine. In preparing a liter of the 2000-mg/l solution of chloramine-T as chlorine, we used 7.945 g of sodium N-chloro-p-toluenesulfonamide trihydrate instead of the 15.882 g specified by Rigdon (6). Rigdon actually used a 4000-mg/l solution of chloramine-T as chlorine for dilution to 4000 μg/l to calibrate for the MC method rather than the 2000-μg/l solution he thought he was using.

The 2000-mg/l solution of calcium hypochlorite as chlorine was prepared by dissolving 4.066 g of calcium hypochlorite (Catalogue Number C-100, Fisher Scientific Company, Fair Lawn, New Jersey), which has an equivalent weight of 35.74, equal to one-fourth its molecular weight of 142.98 as shown by half-reaction in equation 2, in deionized water and diluting the solution to 1000 ml in a volumetric flask:

$$2\ OCl^- + 4\ H^+ + 4\ e^- \rightarrow 2\ Cl^- + 2\ H_2O. \qquad (2)$$

This solution was filtered through a series of 0.45-μm membrane filters (Millipore Corporation, Bedford, Massachusetts), and the filtrate was stored in a borosilicate glass bottle that had been sealed with a cone-shaped, polyethylene-lined screw-cap and wrapped in aluminum foil to protect from decomposition by sunlight. Assay results with 0.0375-N PAO (2) verified that this solution contained 2055 mg/l of total chlorine. Also, our total chlorine assay result of 49.6 percent (w/w) for calcium hypochlorite in the filtrate by titration with 0.0375-N PAO (2) did not agree with that of 74.3 percent (w/w) for the raw powder certified by Fisher Scientific Company.

For the MC method (12,13), the 10 percent (w/v) potassium iodide with 0.01-M sodium hydroxide was prepared by mixing 10 ml of 1-M sodium hydroxide in about 750 ml of deionized water, mixing in 100 g of potassium iodide until it dissolved, and diluting the solution to 1000 ml. The 1-M sodium hydroxide was prepared by dissolving 4.0 g of the salt in deionized water and diluting the solution to 100 ml (CAUTION! Wear gloves and safety goggles. Sodium hydroxide attacks the skin and blinds). This reagent contained 0.01-M sodium hydroxide, as recommended orally by Lester P. Rigdon, Lawrence Livermore Laboratory, Livermore, California, instead of the 0.025-M sodium hydroxide reported in the literature (6). The acetate buffer solution with pH 4.0 for total chlorine determinations by the MC method (6,7) was prepared by dissolving 243 g of sodium acetate trihydrate in about 100 ml of deionized water, stirring in 480 g (455 ml) of glacial acetic acid, and diluting the solution with water to 1000 ml.

For the AT method (2), the pH 4 buffer, the 5 percent (w/v) potassium iodide solution, bottles with eye droppers for dispensing the buffer and iodide solutions, and the 0.00564-N (0.2 mg/ml chlorine) PAO reagent were obtained from Fisher and Porter Company, Warminster, Pennsylvania (9).

DETERMINATION OF TOTAL CHLORINE BY THE MC METHOD

All total chlorine determinations by the MC method were performed automatically by the microprocessor, operated as directed in the preliminary instruction manual from Lawrence Livermore Laboratory (17), under the following conditions: (a) the concentration of the standard solution was 4000 μg/l chloramine-T as chlorine; (b) the number of additions of the standard solution was 120; (c) the volume of each addition of the standard solution was 0.005 ml; (d) the total time to add the standard was 2 min; (e) the temperature of the test solution being analyzed was used; and (f) the volume of test solution was 50 ml (plus the volume of spiking solution used for spiked samples).

A 4000-μg/l solution of chloramine-T as chlorine was used to calibrate the MC instead of a 2000-μg/l solution, because (as explained earlier) the directions published by Rigdon (6,17) for preparing this solution yield a 4000-μg/l solution rather than 2000-μg/l solution.

Assays of samples for total chlorine by the MC method were performed by (a) adding 50.0 ml of sample to a disposable 50-ml polystyrene beaker (Catalogue Number B2718-50, Scientific Products, McGaw Park, Illinois); (b) adding 1 ml of the pH 4 acetate buffer reagent; (c) adding 1 ml of the 10-percent (w/v) potassium iodide in 0.01-M sodium hydroxide reagent; and (d) initiating the stirring, standard addition assay, and display of results as given in the instruction manual (17).

Spiked samples for determination of total chlorine by the MC method were prepared by chlorinating the 50.0-ml sample--after it had been added to the disposable polystyrene beaker but before the reagents were added--with accurately known quantities of chlorine dispensed by micropipettes from standard 12.5-mg/l solutions of chloramine-T, calcium hypochlorite, or both as chlorine to yield the expected concentrations shown in Tables 1 and 3. Before the samples were analyzed, a spiked solution of deionized water containing 50 µg/l of chloramine-T or calcium hypochlorite as chlorine was prepared as shown in Table 1 to verify that the MC method was functioning as expected. These spikes verified the accuracy of calibration of the MC method with the standard solution of 4,000 µg/l chloramine-T as chlorine, which was prepared daily by diluting the stock standard (2 g/l). The stock solution was assayed frequently with PAO to determine if its true concentration had changed. The titer of the 4,000 µg/l chloramine-T was not assayed daily before and after conducting experiments.

The 4000-µg/l solution of chloramine-T as chlorine that was used to calibrate the MC instrument was prepared daily by dispensing with a micropipette the required volume of exactly 2 ml of 2000-mg/l stock standard of chloramine-T as chlorine and then diluting to the mark with deionized water in a 1000 ml volumetric flask. The solutions of chloramine-T and calcium hypochlorite that were used for spiking experiments were prepared daily by (a) delivering with micropipettes the required volume of the stock standard (typically 2.50 ml for 2000 mg/l chloramine-T as chlorine and 2.43 ml for 2055 mg/l calcium hypochlorite as chlorine) and then diluting to the mark with deionized water in a 100 ml volumetric flask to yield a 50-mg/l chlorine solution and (b) diluting 25 ml of the 50-mg/l chlorine solution to 100 ml to yield the 12.5-mg/l chlorine solution.

DETERMINATION OF TOTAL CHLORINE BY THE AT METHOD

All determinations by the AT method were performed as directed in the section of the instruction manual from Fisher and Porter (9) that described the titration for total chlorine.

Spiked samples for determination of total chlorine by the AT method were prepared by chlorinating the 200-ml sample--after it had been added to the plastic sample jar but before the of reagents were added--with accurately known quantities of chlorine dispensed by micropipettes from standard 50-mg/l solutions of chloramine-T, calcium hypochlorite, or both as chlorine to yield the expected concentrations shown in Tables 2 and 4. Before the samples were analyzed, a spiked solution of deionized water containing 249 μg/l of chloramine-T or calcium hypochlorite as chlorine was prepared as shown in Table 2 to verify that the AT method was functioning as expected.

Directions for preparing the 50-mg/l solutions of chloramine-T and calcium hypochlorite as chlorine are given at the end of the section describing the "Determination of Total Chlorine by the MC Method."

In addition to forward amperometric titration by 0.00564-N (0.20 mg/ml chlorine) PAO, as described in the instruction manual from Fisher and Porter (9), titration by 0.001128-N (0.04 mg/ml chlorine) PAO, as recommended by Gerald D. McKee, EMSL, EPA, Cincinnati, Ohio, was attempted to determine whether the sensitivity of the method could be enhanced by using a diluted titrant. Table 6 shows that results that are low by about 15 percent are obtained by titration with 0.001128-N (0.04 mg /ml chlorine) PAO as compared to those obtained by titration with 0.00564-N (0.20 mg/ml chlorine) PAO for assays of a deionized water solution spiked with 249 μg/l of chloramine-T as chlorine. Therefore, titrations with 0.001128-N PAO were abandoned in favor of those with 0.00564-N PAO.

SECTION 5

RESULTS AND DISCUSSION

DEIONIZED WATER

Maximum Concentration Limit

Spiked standard total chlorine solutions were prepared as described in Section 4, Tables 1-4. The concentrations of total chlorine in spiked deionized water sample shown in Tables 7-12 for experimental recoveries by MC and AT methods were the average of the final concentrations listed in Tables 1-2 (for the MC and AT methods) and Tables 3-4 (for the MC and AT methods). Definitions for mean, standard deviation, relative deviation, bias (accuracy) (18), and one-sample t test (19) are given in the literature.

The one-sample t test values reported in Tables 7-12 are useful for assessing the relevance of chemical recovery by applying a t test for determining the difference between the mean values for total chlorine recoveries ("mean recovered") and the amount of chlorine known to have been added (as a "spike") for replicate determinations of total chlorine at 95 percent confidence ($t_{0.025}$- two-tailed for number of replicates minus one). If t (calculated) is greater than t (from table), then the difference is significant. For seven replicates, the t (from table) is 2.45, so t (calculated) values greater than this are significant (19).

These 95 percent confidence limits were used throughout this report.

Experimental recovery of total chlorine from seven replicate analyses of deionized water spiked with chloramine-T for determination of the maximum detection limit of the MC method are shown in Table 7, Experiments 7.4-7.10. For concentrations of 5-100 μg/l total chlorine, shown in Experiments 7.4-7.8, the agreement between spike and mean recovered is acceptable, although about 2 μg/l is lost for the 5- and 10 μg/l spikes and about 10 μg/l is gained for a 100 μg/l spike with a highly significant calculated t value of 15. The slightly high bias of 9.0 percent by the MC method from the seven replicate 100-μg/l spikes with chloramine-T as chlorine (Experiment 7.8) compares favorably with that of 9.0 percent from the seven replicate 100-μg/l spikes with calcium hypochlorite (Experiment 11.6) and with that of 2.0 percent from the seven replicate 100-μg/l spikes with a 50 percent (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine (Experiment 12.5). The maximum concentration limit of 100 μg/l agrees with that of 100 μg/l reported by Rigdon in his original publication (6) but is greater than the 75 μg/l he reported in a subsequent study (7).

This value is much smaller than the maximum detection limit of 20,000 μg/l chlorine for the Orion Research Model 97-70 total chlorine electrode (10) when used without microprocessor calculation of the best value as is done by the MC method (8). For spikes of 247 and 481 μg/l (Experiments 7.9-7.10), the biases of 23.1 and 48.6 percent are judged unacceptable. But results of Experiments 7.11-7.13 showed that dilution (see Table 1 for specific dilutions) of 149, 198, and 247 μg/l spikes, before addition of iodide and acetate reagents and automated standard addition assay (17), yielded truly favorable biases of 2.7, 1.0, and 0.8 percent, respectively.

Interferences

The pH of the test solution may affect the completeness of the reaction between chlorine and iodide, as exemplified by the following reaction:

$$HOCl + 2I^- + H^+ \rightarrow I_2 + Cl^- + H_2O \qquad (3)$$

The results of tests conducted at different pH values are shown in Experiments 8.1-8.5 for experimental recovery, by the MC method, of total chlorine from individual deionized water solutions. These solutions were spiked sequentially with 50 μg/l of chloramine-T as chlorine, and the total chlorine was assayed following the addition of potassium iodide and a series, respectively, of pH 3.6, 3.8, 4.0, 4.2, and 4.4 buffers. As shown by the complete recovery of total chlorine from these buffers, chemical contaminants that affect sample pH, such as sulfuric acid in runoff from abandoned strip mines and metallurgical industry (8), will not interfere with determinations. This assumes the pH of the sample solution falls between pH 3.6 and 4.4 after the addition of the pH 4.0 buffer used to assay for total chlorine.

Chromium(VI) may oxidize potassium iodide, just as total chlorine does, and produce an extraneous source of iodine (2,3,10). Mercury may poison the response of the platinum iodine-iodide sensing element (10). Bromide may also affect the chemistry of the reaction between chlorine and iodide by complex means. However, the results of Experiments 8.6 and 8.8, show that the experimental recovery by the MC method of total chlorine from deionized water spiked with chloramine-T as chlorine is unaffected by 500 μg/l of chromium(VI) (introduced as dichromate), 10 μg/l of mercury(II), and 100 μg/l of bromide. These concentrations of chromium(VI) and mercury(II) are much higher than the total concentrations (sum of all chemical forms) of each metal expected in ash pond effluent waters from coal-burning electric plants (14) and are also higher than the concentrations present in the condenser cooling river water samples shown in Tables 18, 21, 22, 25, and 28. The concentration of bromide tested is about the highest found in sulfur dioxide scrubber solutions, which contain bromide in higher concentrations than river water. The absence of interference from chromium(VI) and mercury(II) with the MC method confirmed the electrode characteristics of the Orion Reserch Model 97-70 total chlorine electrode(10).

Experiments 8.10-8.11 show the effect of zinc(II) on experimental recovery, by the MC method, of total chlorine from deionized water spiked with 50 μg/l of chloramine-T as chlorine.

This total chlorine spike was used in subsequent experiments unless specified otherwise.

While experimental recovery was unaffected by 990 μg/l zinc(II), as evidenced by the 2.6 percent bias in Experiment 8.9, 1000 mg/l zinc(II) (Experiment 8.10) produced very high results (164 percent bias) with a highly significant t value of 13, as compared to the two-tailed $t_{0.025}$ test value of 2.447, and 10 mg/l zinc(II) (Experiment 8.11) gave slightly high results (13.6 percent bias) with a highly significant t value of 13.6 compared to that of 2.6 without zinc(II), as shown in Experiment 7.7. Many condenser cooling river water samples contain small amounts of zinc, as shown by the results in Tables 18, 21, 22, 25, and 28, but should there be a 10-fold increase in concentration in recirculated condenser cooling river water blowdown, the concentration of 1 mg/l of zinc(II) will not be exceeded; thus, no interference will be caused by zinc. For samples with higher concentrations of zinc(II), Experiment 8.12 shows that the spike of 50 μg/l of chloramine-T as chlorine was completely recovered (0 percent bias) when 2 percent (w/v) sodium pyrophosphate decahydrate was added to the sample before the potassium iodide and acetate buffer (pH 4.0) reagents were added. As shown by the stability constants (20), zinc(II) forms a chelated compound with excess pyrophosphate to stop free zinc(II) from reacting with tri-iodide, I_3^{-1}, which predominates in iodine solutions with excess iodide(13), to form unwanted chelated compounds with zinc(II) that cannot be sensed by the platinum iodine-sensing element of the electrode for the MC method. With the AT method, which uses the same iodimetric chemistry as does the MC method, Manabe (15) used 0.1 percent (w/v) pyrophosphate to overcome interference by copper(II) and iron(III), which are chelating metals similar to zinc(II).

The 6.8 percent bias in Experiment 8.13 shows that 500 μg/l of copper(II) slightly affected recovery, by the MC method, of total chlorine from deionized water (6.8 percent bias). With the possible exception of the condenser cooling river water from the Kingston Steam Plant, which contained 120 μg/l copper (Table 18), most of the samples of river water used for condenser cooling contained very small amounts of copper (Tables 21, 22, 25, and 28). Thus, should there be a 10-fold increase in the concentration of copper in recirculated condenser cooling river water blowdown, the concentration of 500 μg/l of copper will not be reached (with the possible exception of the river water at Kingston Steam Plant), and no interference will be caused by copper. At concentrations of 500 and 5 mg/l of copper(II) (Experiments 8.14 and 8.15), recovery was biased by 134 and 34 percent, respectively. Experiment 8.16 shows that the addition of 2 percent (w/v) sodium pyrophosphate decahydrate to a solution containing 5 mg/l copper(II) and 50 μg/l of chloramine-T as chlorine, before the iodide and acetate buffer (pH 4.0) reagents are added to generate iodine, improved total chlorine recovery to -2.6 percent bias. Our results corroborate those obtained by Manabe (15), who used 0.1 percent (w/v) pyrophosphate to overcome interference by copper(II) with the AT method, and those obtained by Orion (10), who warned that copper(II), a strong oxidizing agent, should be excluded from iodimetric methods but did not specify what concentration levels of copper(II) may be tolerated without interference.

The results from Experiments 8.17, 8.19, and 8.21 show, respectively, that 1000 mg/l, 9900 μg/l, and 5 mg/l of iron(III) cause biases of 2680, 24.6, and 8 percent in the experimental recovery, by the MC method, of total chlorine from deionized water. Although the results from Experiment 8.21 show that 5 mg/l of iron(III) produces a significant bias of 8 percent [for example, compare the t value of 8.1 with that of 2.5 for Experiment 7.7 without iron(III)], the river water TVA uses for condenser cooling contains only 0.38-1.6 mg/l iron (Tables 18, 21, 25, and 28). However, a slurry of settled materials from unchlorinated Shawnee condenser outlet water, which contained 8 mg/l of iron (Table 22), produced a small total chlorine value of about 35 μg/l by the MC method (see Experiment 23.1 replicate numbers 6 and 7) as compared to none in the same sample--except without settled materials (see replicate numbers 1-5)--which contained 1.2 mg/l iron (see Table 21).

The concentration of 5 mg/l iron will not be exceeded except in slurries remaining after decantation of supernatants from condenser water samples and in recirculated condenser cooling river water blowdown; therefore, iron(III) will not cause inteference. For river water containing more than 5 mg/l of iron(III), 2 percent (w/v) pyrophosphate decahydrate can be used to overcome most of the interference from 1000 mg/l iron(III) and all interference from 9900 μg/l iron(III) as shown by biases of 11.8 and -1.8 percent in Experiments 8.18 and 8.20, respectively. It should be noted that a bias of 3286 percent was noted when the MC method was used to attempt to recover 50 μg/l of chloramine-T as chlorine from 1000 mg/l iron(III) in deionized water containing 0.4 percent (w/v) sodium pyrophosphate decahydrate. With the exception of the 2 percent (w/v) pyrophosphate concentration that had to be used to eliminate interference by iron(III), these results corroborate those obtained by Manabe (15), who used 0.1 percent (w/v) pyrophosphate to overcome interference from iron(III) with the AT method.

Pyrophosphate was shown to negate interference by concentrations of 10 mg/l zinc(II) (Experiment 8.12), 5 mg/l copper(II) (Experiment 8.16), and 9.9 mg/l iron(III) (Experiment 8.20). Further tests were conducted to determine whether quantitative recovery of total chlorine was affected by pyrophosphate itself. Experiments 10.7 and 10.8 indicate that pyrophosphate was not suitable for overcoming interference by 10 mg/l zinc(II), 5 mg/l copper(II), or 9.9 mg/l iron(III) because it caused biases of -48 and -46 percent for the experimental recovery of total chlorine, by the MC method, from 2 percent (w/v) pyrophosphate in deionized water spiked with 149 and 198 μg/l of calcium hypochlorite as chlorine. The latter two test concentrations are very important because EPA has proposed to limit total chlorine discharges to 140 μg/l (1). These biases (-48 and -46 percent) are lower than those obtained in the absence of pyrophosphate (-1.3 and -1.0 percent, respectively, as shown in Experiments 11.7 and 11.8). These results do not agree with those by Manabe (15), who observed quantitative recovery by the AT method from 0.1 percent (w/v) pyrophosphate in deionized water spiked with 1000 μg/l sodium hypochlorite as chlorine.

The loss of chlorine when 2 percent (w/v) pyrophosphate is spiked with 149 and 198 μg/l of calcium hypochlorite as chlorine may be caused by break-point chlorination products derived from traces of ammonia in the pyrophosphate reagent (6). This possibility was not investigated, but this hypothesis is supported by the absence of grossly low biases for pyrophosphate spiking experiments as compared to those without pyrophosphate for 0, 5, 10, 25, 50, and 100 μg/l of calcium hypochlorite as chlorine (see Experiments 10.1-10.6 and Experiments 11.1-11.6) and for 0, 5, 10, 25, 50, 100, 149, 198, and 247 μg/l of chloramine-T as chlorine (see Experiments 9.1-9.9 and Experiments 7.1, 7.4-7.8, and 7.11-7.13).

Therefore, pyrophosphate needs further study.

Experiment 8.22 shows that 500 μg/l of arsenic(III) produced erratic, generally high recoveries of total chlorine. (The standard deviation was 114 μg/l and the bias was 138 percent by the MC method for deionized water.) In Experiment 8.23, a consistently high bias of 50 percent was caused by 200 μg/l of arsenic(III), and in Experiment 8.24 somewhat low results (-12.8 percent bias) were caused by 50 μg/l of arsenic(III). Apparently, arsenic(III) inhibits or poisons the response of the platinum iodine-sensing element in the Orion Research Model 97-70 total chlorine electrode used for the MC method, although this is not mentioned by Orion (10). In contrast, Experiments 8.25 and 8.26 show no interference from 200 μg/l and 50 μg/l arsenic(V) in the experimental recovery, by the MC method, of total chlorine from deionized water. Thus, arsenic(III) affected experimental recovery, but arsenic(V) had no effect. From a table of standard oxidation-reduction potentials (21), it can be shown, by subtracting appropriate half-reactions, that the potential is +0.67 volt for the following reaction, and that, because of the positive potential, the oxidation of arsenic(III) to arsenic(V) by atmospheric oxygen, which is normally present, proceeds spontaneously:

$$2\ HAsO_2 + 2\ H_2O + O_2 \rightarrow 2\ H_3AsO_4. \qquad (4)$$

This reaction is also independent of pH, so complete oxidation of arsenic (III) to arsenic(V) will occur without effect from the pH of the sample. Because all arsenic will exist as arsenic(V), its interference should be negligible. Turner (22) found that oxidation of arsenic(III) to arsenic(V) is rapid in aerated leachate solutions of fly ashes, although the oxidation rate may be affected by catalysts, such as copper salts and manganese oxide present in such solutions. Also, chemical analysis of condenser cooling river water samples, shown in Tables 18, 21, 22, 25, and 28, revealed a maximum total arsenic concentration of only 6 µg/l, although samples of ash pond water (which is not used for condenser cooling in TVA), may contain total arsenic concentrations as high as 290 µg/l (14).

As shown by Experiment 8.27, 990 µg/l of manganese(VII) produced a very erratic, generally low experimental recovery, by the MC method, of total chlorine from deionized water. Because manganese(VII) is a very strong oxidizing agent, its existence is unlikely in river water, although some manganese dioxide could be present and serve as an oxidant (just as chlorine does) to produce iodine in the iodimetric reaction (10). The total manganese concentrations in the condenser cooling river water samples analyzed for this study were 50-670 µg/l (Tables 18, 21, 22, 25, and 28).

Precision, Accuracy, and Minimum Detection Limit for Spikes with Chloramine-T

Chloramine-T is a source of combined chlorine. It slowly liberates hypochlorous acid on contact with water (23). It simulates a combined source of chlorine, such as monochloramine or dichloramine, that exists in chlorinated condenser cooling river water containing ammonia at coal-burning electric power plants (8).

Table 7, Experiments 7.1-7.8 and 7.11-7.13, gives the results of experimental recoveries, by the MC and AT methods, of total chlorine from seven replicate deionized water solutions spiked with 0, 1.25, 2.5, 5, 10, 25, 50, 100, 149, 198, and 247 µg/l of chloramine-T as chlorine. No values below 20 µg/l of total chlorine could be determined by the AT method because one drop (0.02 ml) of 0.00564-N PAO from the 1-ml buret (the minimum amount that could be dispensed during an amperometric titration) represents 20 µg/l of total chlorine when a 200 ml sample is titrated by the standard method (2-4,9). For experimental recovery of total chlorine from spiked deionized water, by the MC and AT methods, Table 7 shows the total chlorine spike of chloramine-T as chlorine, the mean total chlorine, the total chlorine standard deviation, the relative standard deviation, the bias (accuracy), and a calculated t value to test for significance of total chlorine recovered (18,19).

For the MC method, Figures 1-3 summarize different combinations of paired values shown in Table 7: total chlorine standard deviation against mean total chlorine, relative standard deviation against mean total chlorine, mean bias against total chlorine concentration added. Figures 4-6 show analogous summaries for the AT method.

In chlorine discharge and minimization studies, the usual concentration range of interest is 0-200 µg/l of total chlorine (4). In fact, EPA recently proposed that total chlorine discharges to surface waters be limited to 140 µg/l (1), and recent collaborative tests of the AT method reported standard deviations that were obtained by averaging values over

0-200 μg/l (4). In light of these considerations and the limiting measurable concentration of 20 μg/l of total chlorine by the AT method, standard deviations were pooled (19), relative standard deviations were averaged, and biases were averaged for the recoveries by the AT method (Table 7) over the mean total chlorine concentration range of from 20 to 200 μg/l. For comparison with the AT method, the same averages for the MC method were calculated over mean total chlorine concentrations of 20-200 μg/l; and because of the reported minimum detection limit of about 2 μg/l of total chlorine (values of 3 and 4 μg/l were actually reported) by the MC method (6,7), averages were also computed over mean total chlorine concentrations from 2 to (but not including) 20 μg/l.

This procedure for averaging values of 2-20 μg/l and 20-200 μg/l was used throughout this report.

Experimental recoveries, by the MC method, of total chlorine from deionized water spiked with chloramine-T as chlorine yielded a total chlorine pooled standard deviation of 0.4 μg/l, a mean percent relative standard deviation of 10.5 percent, and a mean bias of -21.2 percent for concentrations of 2-20 μg/l (Experiments 7.3-7.5) and a total chlorine pooled standard deviation of 2.9 μg/l, a mean relative standard deviation of 2.1 percent, and a mean bias of 2.2 percent for concentrations of 20-200 μg /l (Experiments 7.6-7.8 and 7.11-7.12). The statistical values determined by the MC method for 20-200 μg /l are similar to those reported by Rigdon (6), but values for 2-20 μg /l are several times larger. For the AT method, for concentrations of 20-200 μg /l, the experimental recoveries with chloramine-T showed a total chlorine pooled standard deviation of 4.0 μg/l, a mean relative standard deviation of 4.6 percent, and a mean bias of 2.6 percent (Experiments 7.6-7.8 and 7.11-7.12). These values compare favorably with those determined by the MC method (2.9 μg/l, 2.1 percent, and 2.2 percent).

A procedure being developed by EPA (24) allows the minimum detection limit (MNDL) for the MC method to be calculated from the standard deviations of the data for experimental recovery of very low concentrations of total chlorine (for example, 1.25, 2.5, 5 and 10 μg /l, for the seven replicate deionized water spikes with chloramine-T shown in Experiments 7.2-7.5). For example, from the standard deviation for the 2.5-μg /l spikes (Experiment 7.3), the minimum detection limit (MNDL) can be calculated by means of the following equation:

$$\mathrm{MNDL} = t_{(n-1,\ 0.99)}\,(\mathrm{SD}), \tag{5}$$

where, $t_{(n-1,\ 0.99)}$ = t value for 99 percent confidence level (one-tailed) with n-1 degrees of freedom (the number of replicate analyses minus one), and, SD = standard deviation of the replicate analyses.

For the seven replicate analyses shown in Experiment 7.3, the appropriate t value is $t_{6,\ 0.99}$ = 3.143 (19,24). Substituting the SD value of 0.38 μg/l from Experiment 7.3 and t = 3.143 into equation 5 yields a MNDL of 1.2 μg/l.

The 95 percent confidence interval estimate for the 1.2 μg/l MNDL can be estimated from the following equations:

$$\mathrm{LCL} = 0.64\ \mathrm{MNDL} \tag{6}$$

and

$$\mathrm{UCL} = 2.20\ \mathrm{MNDL}, \tag{7}$$

where LCL and UCL are the lower and upper 95 percent confidence limits, respectively, based on seven replicate analyses.

The right-hand members of equations 6 and 7 were derived by multiplying the MNDL by the reciprocal of the result obtained by taking the square-root of the chi-squared distribution values divided by the degrees of freedom for the 0.975 and 0.025 probabilities, respectively,

$\mathrm{MNDL} \Big/ \sqrt{\frac{14.449}{6}}$ and $\mathrm{MNDL} \Big/ \sqrt{\frac{1.237}{6}}$ (18,25).

Substitution of the 1.2 μg/l MNDL into equations (6) and (7) yields an LCL of 0.77 and a UCL of 2.64. Since the mean total chlorine of 2.23 μg/l recovered in Experiment 7.3 falls within the LCL and UCL, there is no good reason to reject the MNDL of 1.2 μg/l as a good estimate, because when this occurs, it is assumed that the variability comes from measurements of total chlorine within the range of concentrations where it is first detected. Thus, the mean recovery is consistent with the UCL and LCL of the MNDL. The MNDL of 1.2 μg/l for the MC method for deionized water spiked with chloramine-T is lower than the 3- and 4-μg/l values that Rigdon estimated for the MC method by spiking deionized water with chloramine-T (6,7).

Although an MNDL for the MC method can be calculated, too, for each set of the seven 1.25, 5, and 10 μg/l deionized water spikes with chloramine-T as chlorine shown in Table 7, Experiments 7.2 and 7.4-7.5, none of the mean total chlorine concentrations recovered falls within the LCL and UCL for the MNDL. For example, the MNDL calculated from the 1.25 μg/l spikes in Experiment 7.2 yields a mean total chlorine concentration recovered that falls below the LCL. This means try a higher spike. The MNDL values calculated from the 5- and 10-μg/l chlorine spikes in Experiments 7.4 and 7.5 give mean total chlorine concentrations that are above the UCL. This means try a lower spike. It turns out that the optimum spike for determining the MNDL was 2.5 μg/l chlorine (Experiment 7.3), because this yielded a mean total chlorine concentration within the LCL and UCL.

This procedure for determining the MNDL was used throughout this report.

It was not possible to make a good estimate of the MNDL for the AT method from the 25 μg/l spikes of chloramine-T as chlorine shown in Table 7, Experiment 7.6, because the mean total chlorine was above the UCL.

Precision Accuracy, and Minimum Detection Limit for Spikes with Calcium Hypochlorite

Calcium hypochlorite, a chemical compound largely used as a source of hypochlorite, represents the usual source of free chlorine employed for disinfecting water (8); therefore, it simulates the chlorine source used as a biocide in condenser cooling river water at coal-burning electric plants (4).

Table 11, Experiments 11.1-11.9, gives experimental recoveries, by the MC and AT methods, of total chlorine from seven replicate deionized water solutions spiked with 0, 5, 10, 25, 50, 100, 149, 198, and 247 μg/l of calcium hypochlorite as chlorine.

For the MC method, Figures 7-9 summarize different combinations of paired values shown in Table 11: total chlorine standard deviation against mean total chlorine, relative standard deviation against mean total chlorine, and mean bias against total chlorine concentration added. Figures 10-12 show similar summaries for the AT method.

The experimental recoveries, by the MC method, of total chlorine from deionized water spiked with calcium hypochlorite as chlorine (Table 11) yield a total chlorine pooled standard deviation of 0.5 μg/l, a mean relative standard deviation of 9.8 percent, and a mean bias of -23.8 percent for concentrations of 2-20 μg/l (Experiments 11.2-11.3) and a total chlorine pooled standard deviation of 4.7 μg/l, a mean relative standard deviation of 4.4 percent, and mean bias of -1.0 percent for concentrations of 20-200 μg/l (Experiments 11.4-11.8). The statistical values determined by the MC method for 20-200 μg/l chlorine in standards spiked with calcium hypochlorite are similar to those with chloramine-T by Rigdon (6), but values for 2-20 μg/l are several times larger. Over the concentration range of 2-200 μg/l, the statistical values determined by the MC method with calcium hypochlorite spikes are similar to those with the chloramine-T spikes, although the standard and relative standard deviations for the calcium hypochlorite spikes are slightly higher for concentrations of 20-200 μg/l.

For the AT method over concentrations of 20-200 μg/l, the experimental recoveries with calcium hypochlorite give a total chlorine pooled standard deviation of 4.3 μg/l, a mean relative standard deviation of 6.4 percent, and mean percent bias of -1.0 percent (Experiments 11.4-11.8). These values compare favorably with those determined by the MC method (4.7 μg/l, 4.4 percent, and -1.0 percent, respectively).

The MNDL can be calculated for the MC and AT methods from results in Table 11 for experimental recovery from deionized water spiked with calcium hypochlorite. A good estimate of MNDL cannot be calculated for the MC method because the mean recovery of 3.66 μg/l for the 5-μg/l spike (Experiment 11.2) was above the UCL of the MNDL.

However, two valid estimates of the MNDL for the AT method are 11.9 and 15.1 μg/l which come from the results of Experiments 11.3 and 11.4. The standard deviations from Experiments 11.3 and 11.4 can be combined (19) to yield a pooled MNDL of 11.5 μg/l for the AT method with a pooled mean recovery of 18.9 μg/l.

Precision, Accuracy, and Minimum Detection Limit for Spikes with 50 Percent (w/w) Mixture of Calcium Hypochlorite and Chloramine-T as Chlorine

Calcium hypochlorite simulates a source of free chlorine used as a biocide in condenser cooling river water (4,8), and chloramine-T simulates a source of combined chlorine, such as monochloramine, which may be present in chlorinated condenser cooling water containing ammonia (8). Therefore, the mixture of both calcium hypochlorite and chloramine-T used for spiking provides a synthetic mixture of simulated free and combined chlorine species found in some chlorinated condenser waters.

Table 12, Experiments 12.1-12.9, gives experimental recoveries by the MC and AT methods of total chlorine from seven replicate deionized water solutions spiked with 0, 10, 20, 50, 100, 149, 198, 247, and 488 μg/l of a 50 percent (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine.

For the MC method, Figures 13-15 summarize different combinations of paired values shown in Table 12: total chlorine standard deviation against mean total chlorine, relative standard deviation against mean total chlorine, and mean bias against total chlorine concentration added. Figures 16-18 show similar summaries for the AT method.

The experimental recoveries by the MC method of total chlorine from deionized water spiked with a 50 percent (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine (Table 12) yield a total chlorine pooled standard deviation of 0.8 μg/l, a mean relative standard deviation of 4.9 percent, and a mean bias of -5.5 percent for concentrations of 2-20 μg/l chlorine (Experiments 12.2-12.3) and a total chlorine pooled standard deviation of 10.0 μg/l, a mean relative standard deviation of 6.1 percent, and a mean bias of -2.7 percent for concentrations of 20-200 μg chlorine/l (Experiments 12.4-12.6). The statistical values determined by the MC method for 20-200 μg/l chlorine in standards spiked with a 50 percent (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine are slightly higher than those with chloramine-T by Rigdon (6), but values for 2-20 μg/l chlorine are several times larger.

For the concentration range of 2-200 μg/l chlorine, the statistical values of pooled standard deviation, mean relative standard deviation, and mean bias by the MC method with the 50 percent (w/w) spikes of calcium hypochlorite and chloramine-T as chlorine are similar to those with the individual spikes of chloramine-T and calcium hypochlorite except that the standard and relative standard deviations for the spiked mixture of calcium hypochlorite and chloramine-T are somewhat higher for concentrations of 20 and 200 μg/l chlorine.

For the AT method, for concentrations of 20-200 μg/l chlorine, the experimental recoveries with a 50 percent (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine (Table 12) give a total chlorine pooled standard deviation of 3.4 μg/l, a mean relative standard deviation of 3.4 percent, and a mean bias of -0.8 percent (Experiments 12.4-12.6). These values determined by the AT method are about one-half those determined by the MC method (10.0 μg/l, 6.1 percent, and -2.7 percent, respectively). For concentrations of 20-200 μg/l chlorine, the statistical values of pooled standard deviation, mean relative standard deviation, and mean bias by the AT method with the 50 percent (w/w) spikes of calcium hypochlorite and chloramine-T as chlorine are about the same as those with the individual chloramine-T and calcium hypochlorite spikes.

The MNDL for the MC and AT methods can be calculated from results in Table 12 for experimental recovery from deionized water spiked with a 50 percent (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine. An accurate estimate of MNDL cannot be calculated for the MC method because the mean recovery of 9.10 μg/l for the 10-μg/l spike (Experiment 12.2) was above the UCL of the MNDL. But a valid estimate of 16.7 μg/l can be calculated for the MNDL by the AT method from the results of Experiment 12.3, which showed a mean recovery of 14.3 μg/l.

Overall Precision, Accuracy, and Minimum Detection Limit for Spikes with Chloramine-T, Calcium Hypochlorite, and Both

The pooled standard deviations, mean relative standard deviations, and mean biases for the MC and AT methods for each of the three spiking experiments with chloramine-T, calcium hypochlorite, and both in deionized water can be averaged to yield overall values.

For the MC method, the total chlorine overall pooled standard deviation is 0.5 μg/l, the overall mean relative standard deviation is 8.7 percent, and the overall mean bias is -17.5 percent for concentrations of 2-20 μg/l chlorine (Table 7, Experiments 7.3-7.5; Table 11, Experiments 11.2-11.3; and Table 12, Experiments 12.2-12.3), and the total chlorine overall pooled standard deviation is 5.9 μg/l, the overall mean relative standard deviation is 3.9 percent, and the overall mean bias is -0.2 percent for concentrations of 20-200 μg/l chlorine (Table 7, Experiments 7.6-7.8 and 7.11-7.12; Table 11, Experiments 11.4-11.8; and Table 12, Experiments 12.4-12.6). The overall statistical values for the MC method for 20-200 μg/l chlorine in standards spiked with chloramine-T, calcium hypochlorite, and both are slightly higher than those with chloramine-T reported by Rigdon (6), but values for 2-20 μg/l chlorine are several times greater. The overall mean bias of -17.5 percent means that a true concentration of total chlorine cannot be established at concentrations of 2-20 μg/l in deionized water because it is not a conserved species (some of it is lost by decomposition to chemical species that are not measured by the MC analytical procedure).

For the AT method, for concentrations of 20-200 μg/l, the total chlorine overall pooled standard deviation is 4.0 μg/l, the overall mean relative standard deviation is 5.0 percent, and the overall mean bias is 0.5 percent (Table 7, Experiments 7.6-7.8 and 7.11-7.12; Table 11, Experiments 11.4-11.8; and Table 12, Experiments 12.4-12.6). These values are about the same as those for the MC method (5.9 μg/l, 3.9 percent, and -0.2 percent, respectively).

The overall pooled MNDL can be calculated for the MC and AT methods by combining the respective pooled or individual MNDL values from each of the three spiking experiments with chloramine-T, calcium hypochlorite, and both. For the MC method, the overall MNDL is 1.2 μg/l, which is the same as the MNDL for spiking with chloramine-T in Experiment 7.3, in which the mean total chlorine of 2.23 μg/l was recovered. This was the only valid MNDL generated for the MC method in deionized water media. This MNDL is lower than the of 3- and 4-μg/l values estimated by Rigdon (6,7) from spiking experiments with chloramine-T in deionized water. However, a valid overall pooled MNDL of 12.0 μg/l can be calculated for the AT method from the results of Experiments 11.3, 11.4, and 12.3, which yield an overall, pooled mean recovery of 17.4 μg/l.

RIVER WATER

Precision and Minimum Detection Limit for Spikes with Chloramine-T

Table 13 shows the chlorine demand characteristics of a raw Ross Landing surface river water sample (chlorinated at particular concentrations for specified periods of time) that was used for spiking experiments with chloramine-T, and Table 14 shows its concentrations of inorganic species, sanitary chemical characteristics, and physical properties. Spiking with chloramine-T simulates a combined source of chlorine, such as monochloramine, that exists in chlorinated condenser cooling river water containing ammonia at coal-burning electric power plants (8).

Table 15, Experiments 15.1-15.11, shows experimental recoveries, by the MC and AT methods, of total chlorine from seven replicate river water solutions that were spiked with 50, 55, 60, 75, 99, 148, 197, 245, and 295 μg/l chloramine-T as chlorine for the MC method and with 50, 55, 60, 75, 100, 150, 199, 249, and 299 μg/l chloramine-T as chlorine for the AT method. Comparison of the mean total chlorine recoveries by the MC and AT methods from river water spiked with the total chlorine concentrations (Table 15) shows that 10-30 percent of the chlorine in chloramine-T spikes is lost after spiking without delay before analysis. This loss, which is probably due to chlorine demand, is evident in river water even at concentrations between 20 and 200 μg/l whereas this loss does not occur in deionized water, as shown by Table 7, Experiments 7.6-7.8 and 7.11-7.12. Apparently a true concentration of total chlorine in river water cannot be established by spiking with accurately known amounts of total chlorine in the form of chloramine-T, because some of it is lost by reaction with substances in the water to form chemical species that are not measured by the MC and AT analytical methodology. Therefore, the true recoveries of the chloramine-T spikes were not evaluated.

For the MC method, Figure 19 summarizes total chlorine standard deviation against mean total chlorine for data taken from Table 15, Experiments 15.2-15.11, and Figure 20 summarizes relative standard deviation against mean total chlorine concentration. Figures 21-22 similarly summarize the statistical results for the AT method.

The experimental recoveries, by the MC method, of total chlorine from river water spiked with chloramine-T (Table 15) yield a total chlorine pooled standard deviation of 2.3 μg/l and mean relative standard deviation of 2.5 percent for concentrations of 20-200 μg/l (Experiments 15.2-15.8). Although no data were obtained for concentrations of 2-20 μg/l, the total chlorine pooled standard deviation of 2.3 μg/l and mean relative standard deviation of 2.5 percent for concentrations of 20-200 μg/l in river water are similar to those found by Rigdon (6,7) in deionized water.

For the AT method, for concentrations of 20-200 μg/l, the results in Table 15 show a total chlorine pooled standard deviation of 4.1 μg/l and a mean relative standard deviation of 7.8 percent (Experiments 15.5-15.8). These values are about twice those for the MC method (2.3 μg/l and 2.5 percent, respectively).

An accurate estimate of MNDL in river water cannot be calculated for the MC method from the data in Table 15 because the mean recovery of 28.0 μg/l for the lowest chloramine-T spike of 50 μg/l (Experiment 15.2) was greatly above the UCL of the MNDL. However, three valid estimates of the MNDL in river water can be calculated for the AT method from the results of Experiments 15.2, 15.4, and 15.5. The MNDL values are 11.9, 16.7, and 15.1 μg/l for mean recoveries of 11.4, 15.7, and 28.6 μg/l, respectively. These three MNDL values could not be pooled to obtain a valid pooled MNDL because the pooled mean recovery value was larger than the UCL.

Precision, Accuracy, and Minimum Detection Limit for Spikes with Calcium Hypochlorite

Table 16, Experiments 16.1-16.8, shows experimental recoveries, by the MC and AT methods, of total chlorine from seven replicate river water solutions, characterized by results shown in Tables 13 and 14, that were sequentially spiked with 15, 30, 55, 80, 129, 202, 344, and 383 μg/l calcium hypochlorite as chlorine for the MC method and with 25, 50, 90, 125, 180, 249, 304, and 434 μg/l calcium hypochlorite as chlorine for the AT method. Spiking with calcium hypochlorite simulates free chlorine that exists in chlorinated condenser cooling river at coal-burning electric power plants (8). Because 30-60 percent of the chlorine in the calcium hypochlorite spikes is lost in samples analyzed immediately after spiking (see Table 16), the total chlorine is not conserved. Therefore, evaluation of true chlorine recoveries was abandoned.

For the MC method, Figure 23 summarizes total chlorine standard deviation against mean total chlorine for data taken from Table 16, Experiments 16.2-16.8, and Figure 24 summarizes relative standard deviation against mean total chlorine concentration. Figures 25-26 similarly summarize the statistical results for the AT method.

For the MC method, the experimental recoveries of total chlorine from river water spiked with calcium hypochlorite (Table 16) yield a total chlorine pooled standard deviation of 0.5 μg/l and mean a relative standard deviation of 4.8 percent for concentrations of 2-20 μg/l (Experiment 16.2) and a total chlorine pooled standard deviation of 2.3 μg/l and a mean relative standard deviation of 2.2 percent for concentrations of 20-200 μg/l (Experiments 16.3-16.7). These values (2.3 μg/l and 2.2 percent) for river water spiked with calcium hypochlorite are nearly identical to those for river water spiked with chloramine-T (2.3 μg/l and 2.5 percent). These results are similar to those obtained by Rigdon (6,7) for deionized water spiked with chloramine-T.

For the AT method, for concentrations of 20-200 μg/l, the results in Table 16 can be combined to yield a total chlorine pooled standard deviation of 3.7 μg/l and a mean relative standard deviation of 5.2 percent (Experiments 16.3-16.7). These values (3.7 μg/l and 5.2 percent) for river water spiked with calcium hypochlorite are about the same as those for river water spiked with chloramine-T (4.1 μg/l and 7.8 percent).

A valid MNDL for the MC and AT methods could not be calculated from the data shown in Table 16 for river water spiked with calcium hypochlorite because the mean recoveries of 9.59 and 28.6 μg/l from Experiments 16.2 and 16.3, respectively, were greatly above the UCL of the MNDL. No spiking tests were conducted at lower concentrations.

Overall Precision, and Minimum Detection Limit for Spikes with Chloramine-T and Calcium Hypochlorite

The pooled standard deviations and mean relative standard deviations for the MC and AT methods can be combined for the spiking experiments with chloramine-T and calcium hypochlorite in river water to yield overall values.

For the MC method, the total chlorine overall pooled standard deviation is 0.5 μg/l and the overall mean relative standard deviation is 4.8 percent for concentrations of 2-20 μg/l (Table 16, Experiment 16.2). The total chlorine overall pooled standard deviation is 2.3 μg/l and the overall mean relative standard deviation is 2.4 percent for concentrations of 20-200 μg/l (Table 15, Experiments 15.2-15.8; Table 16, Experiments 16.3-16.7). The overall statistical values for the MC method for spiked river water are about the same as those for spiked deionized water.

For the AT method, for concentrations of 20-200 μg/l in spiked river water, the total chlorine overall pooled standard deviation is 3.9 μg/l and the overall mean relative standard deviation is 6.3 percent (Table 15, Experiments 15.5-15.8; and Table 16, Experiments 16.3-16.7). These overall statistical values for the AT method are about twice those for the MC method.

No valid overall MNDL could be determined for either the MC or the AT method from the experimental data in Tables 15 and 16 because the mean recoveries were greater than the UCL. However, three individual MNDL values of 11.9, 16.7, and 15.1 μg/l (which could not be combined) were calculated for the AT method from replicate determinations of river water spiked with chloramine-T. These were the only valid MNDL values that could be computed from the experimental recoveries for river water spiked with chloramine-T or calcium hypochlorite.

CONDENSER COOLING RIVER WATER

Precision and Minimum Detection Limit for Unspiked, Chlorinated Kingston Steam Plant Water Samples

Table 17 shows the chlorine demand characteristics of unchlorinated river water used for condenser cooling at Kingston Steam Plant chlorinated at particular concentrations for specified periods of time and Table 18 shows its concentrations of inorganic species, sanitary chemical characteristics, and physical properties. As shown in Table 18, copper (120 μg/l) and iron (890 μg/l) are only metals present in a sufficiently high concentration to warrant a check against possible interference. However, there should be no interference from either copper or iron at these concentrations, as indicated by experimental recoveries from the spiked deionized water solutions (Table 8, Experiments 8.13 and 8.21).

Table 19, Experiments 19.1, 19.2, 19.4, 19.6, 19.8, and 19.10, shows recoveries by the MC and AT methods for seven replicate determinations of total chlorine in a series of six split samples of unspiked, chlorinated condenser cooling river water from the Kingston Steam Plant with total chlorine concentrations of 0-200 μg/l. The specific composition of each unspiked chlorinated sample is given in Table 19 for each of the experiments. Each sample discussed here and herinafter was analyzed for the seven split, replicate total chlorine determinations by the MC and AT methods when total chlorine determinations by the AT method agreed within 10 percent between analyses.

This procedure for determining when to begin the split, replicate total chlorine determinations was used throughout this report.

For the MC method, Figure 27 summarizes total chlorine standard deviation against mean total chlorine for values from Table 19, Experiments 19.1, 19.2, 19.4, 19.6, 19.8, and 19.10, and Figure 28 summarizes relative standard deviation against mean total chlorine concentration. Figures 29-30 show similar summaries of the statistical results for the AT method.

For the MC method, experimental recoveries of total chlorine from unspiked, chlorinated condenser cooling river water from the Kingston Steam Plant (Table 19) yield a total chlorine pooled standard deviation of 0.8 μg/l and a mean relative standard deviation of 10.8 percent for concentrations of 2-20 μg/l chlorine (Experiments 19.1-19.2); and a total chlorine pooled standard deviation of 4.9 μg/l and mean relative standard deviation of 5.0 percent for concentrations of 20-200 μg/l chlorine (Experiments 19.4, 19.6, 19.8, and 19.10). These values are about equal to overall values for spiked, deionized water. They are about twice those for spiked river water and those Rigdon (6,7) obtained using deionized water.

For the AT method, the results in Table 19 yield a total chlorine pooled standard deviation of 6.4 μg/l and a mean relative standard deviation of 9.5 percent for concentrations of 20-200 μg/l chlorine (Experiments 19.4, 19.6, 19.8, and 19.10). These values are slightly higher than those for the MC method (4.9 μg/l and 5.0 percent, respectively). The total chlorine pooled standard deviation of 6.4 μg/l for the AT method for concentrations of 20-200 μg/l is smaller than that of 28 μg/l for the same concentration range found by a collaborative test in which the sampling, kinds of samples, and variability between operators were included (4).

The MNDL for the MC method for samples of river water used for condenser cooling at Kingston Steam Plant is 2.0 μg/l with a mean recovered concentration of 4.27 μg/l (Table 19, Experiment 19.1), well within the UCL and LCL. For the AT method, the MNDL is 23.6 μg/l with a mean recovered concentration of 51.4 μg/l (Table 19, Experiment 19.6), just barely below the UCL. That means that a lower test concentration should give a better, probably lower, estimate of the MNDL; however, a calculation of the MNDL from data showing a lower mean recovery of 27.9 μg/l (Table 19, Experiment 19.4), failed to yield LCL and UCL values that bracketed this recovery.

For the MC method, the MNDL of 2.0 μg/l chlorine in condenser river water at Kingston Steam Plant compares well with the MNDL of 1.2 μg/l in deionized water, but for the AT method, the MNDL of 23.6 μg/l is higher than the overall pooled MNDL of 12.0 μg/l in deionized water and the individual values of 11.9, 16.7, and 15.1 μg/l for the MNDL in river water.

From the analytical results for split samples of condenser water with concentrations of 20-200 μg/l (Table 19, Experiments 19.4, 19.6, 19.8, and 19.10), a t value can be calculated from the mean for differences ("X" - "Y") between the paired values by the MC and AT methods (the MC method is taken as "X" and the AT method is taken as "Y"). This t value can be compared to the tabulated value of t at the 0.025 level for the number of paired values less one, called the degree of freedom, to check whether the mean differs from zero at 95 percent significance (19,25). Because the absolute value for the calculated t of -1.515 is less than that of 2.052 for 27 degrees of freedom, there is no reason to conclude the mean differs from zero at 95 percent significance. Also, the mean differences between the MC and AT methods was -3.4 μg/l with standard deviation of 12.0 μg/l.

Precision, Accuracy, and Minimum Detection Limit for Spiked, Chlorinated, Kingston Steam Plant Water Samples

Table 19, Experiments 19.3, 19.5, 19.7, 19.9, and 19.11, shows the total chlorine recoveries from the chlorinated Kingston Steam Plant samples shown in Experiments 19.2, 19.4, 19.6, 19.8, and 19.10 after they had been spiked with calcium hypochlorite and the mean background concentration of the unspiked sample had been subtracted. Accuracy calculations were not attempted on recoveries from spiked condenser water from this steam plant or any one discussed hereinafter for the same reasons already given in the discussion of experiments with river water. Furthermore, results obtained by spiking water already chlorinated will probably be biased due to the changes in chlorine damand, which would require correction for the changing chlorine demand of the water. Also, no paired-sample t-tests were attempted for the spiked condenser water samples from this steam plant or any one discussed hereinafter because the spiked concentration of calcium hypochlorite differed for the MC and AT methods. (The spiked concentrations differed for each method in attempts to spike at a concentration to double the background concentration of total chlorine for determinations of the subsequent seven replicates.)

For the MC method, Figure 31 summarizes total chlorine standard deviation against mean total chlorine in spiked condenser water (Table 19, Experiments 19.3, 19.5, 19.7, 19.9, and 19.11), and Figure 32 summarizes relative standard deviation against mean total chlorine concentration. Figures 33-34 similarly summarize the statistical data for the AT method.

For the MC method, experimental recovery of total chlorine from spiked condenser cooling water from Kingston Steam Plant (Table 19) yield a total chlorine pooled standard deviation of 1.0 μg/l and a mean percent relative standard deviation of 8.8 percent for concentrations of 2-20 μg/l chlorine (Experiment 19.3) and a total chlorine pooled standard deviation of 9.2 μg/l and a mean relative standard deviation of 10.1 percent for concentrations of 20-200 μg/l chlorine (Experiments 19.5, 19.7, 19.9, and 19.11).

For the AT method, the results in Table 19 yield a total chlorine pooled standard deviation of 5.5 μg/l and a mean relative standard deviation of 7.8 percent (Experiments 19.5, 19.7, 19.9, and 19.11) for concentrations of 20-200 μg/l chlorine. These values are somewhat lower than those for the MC method (9.2 μg/l and 10.1 percent, respectively).

The MNDL of the MC and AT methods could not be calculated because the mean recoveries of 11.3 and 22.9 μg/l chlorine, respectively, were the lowest recoveries for spiked condenser water at Kingston Steam Plant (Experiments 19.3 and 19.5) and were above the UCL for each respective MNDL.

Precision and Minimum Detection Limit for Unspiked, Chlorinated Shawnee Steam Plant Water Samples

Table 20 shows the chlorine demand characteristics of unchlorinated river water used for condenser cooling at Shawnee Steam Plant chlorinated at particular concentrations for specified periods of time, and Table 21 shows its concentrations of inorganic species, sanitary chemical characteristics, and physical properties. The concentration of 1200 μg/l for iron (Table 21) is sufficiently high to warrant investigation of possible interference. However, there should be no inteference from iron at this concentration, as shown by experimental recoveries from the spiked deionized water solutions (Table 8, Experiment 8.21). After the insoluble materials in the sample shown in Table 21 settled and aliquots of the supernant were withdrawn for diluting chlorinated samples, the settled materials had been concentrated to yield a water slurry with the concentrations of inorganic species shown in Table 22. This solution contained 8000 μg/l of iron, which is sufficiently high to cause interference, as shown by recoveries from spiked deionized water solutions (Experiment 8.19). This fact was confirmed by determinations of 32.3 and 37.7 μg/l chlorine by the MC method for the slurry of settled materials; these concentrations could not be corroborated by the AT method (Table 23, Experiment 23.1, Replicate Numbers 6 and 7).

Table 23, Experiments 23.1, 23.2, 23.4, 23.6, 23.8, and 23.10, shows recoveries by the MC and AT methods for seven replicate determinations of total chlorine in a series of six split samples of unspiked, chlorinated condenser cooling river water from the Shawnee Steam Plant with total chlorine concentrations of 0-200 μg/l. The specific composition of each unspiked, chlorinated sample is given in Table 21.

For the MC method, Figure 35 summarizes total chlorine standard deviation against mean total chlorine for values from Table 23, Experiments 23.2, 23.4, 23.6, 23.8, and 23.10, and Figure 36 summarizes relative standard deviation against mean total chlorine concentration. Figures 37-38 similarly summarize the statistical results for the AT method.

For the MC method, the experimental recoveries of total chlorine from unspiked, chlorinated condenser cooling river water from Shawnee Steam Plant

(Table 23) yield a total chlorine pooled standard deviation of 4.5 µg/l and mean relative standard deviation of 56.9 percent for concentrations of 2-20 µg/l chlorine (Experiment 23.2) and a total chlorine pooled standard deviation of 7.9 µg/l and mean relative standard deviation of 6.8 percent for concentrations of 20-200 µg/l chlorine (Experiments 23.4, 23.6, 23.8, and 23.10). The values of total chlorine pooled standard deviation and mean percentage relative standard deviation for chlorinated water from Shawnee Steam Plant are much higher for concentrations of 2-20 µg/l chlorine than those for chlorinated water from Kingston Steam Plant, but the same values are only slightly greater for concentrations of 20-200 µg/l chlorine.

For the AT method, the results in Table 23 yield a total chlorine pooled standard deviation of 9.9 µg/l and a mean relative standard deviation of 14.3 percent (Experiments 23.4, 23.6, 23.8, and 23.10) for concentrations of 20-200 µg/l chlorine. As was the case for the sample from Kingston, these values are slightly larger than those for the MC method (7.9 µg/l and 6.8 percent, respectively).

The MNDL for the MC method for samples of river water used for condenser cooling at Shawnee Steam Plant could not be calculated because the mean recoveries of 0.0200 and 7.91 µg/l for Experiments 23.1 and 23.2 was below the LCL of both MNDL values. For the AT method, two valid estimates of the MNDL can be calculated. The MNDL values are 22.0 and 25.5 µg/l for mean recoveries of 32.9 and 47.9 µg/l, respectively (Experiments 23.4 and 23.6). Pooling these values failed to yield a valid pooled MNDL for the AT method because the pooled mean recovery of 40.4 µg/l fell outside the UCL. The MNDL values for the AT method for unspiked Shawnee condenser cooling river water are similar to those for unspiked Kingston condenser cooling river water.

A t value can be calculated from the split sample data by the MC and AT methods covering concentrations of 20-200 µg/l chlorine shown in Table 23, Experiments 23.4, 23.6, 23.8, and 23.10. Because the calculated t of 1.095 is less than that of 2.052 for t 0.025 with 27 degrees of freedom, there is no reason to conclude the mean of the differences between the MC and AT methods differs from zero at 95 percent significance. Also, the mean difference was 3.7 µg/l with a standard deviation of 17.8 µg/l.

Precision and Minimum Detection Limit for Spiked, Chlorinated Shawnee Steam Plant Water Samples

Table 23, Experiments 23.3, 23.5, 23.7, 23.9, and 23.11, shows the total chlorine recoveries from the chlorinated Shawnee Steam Plant samples shown in Experiments 23.2, 23.4, 23.6, 23.8, and 23.10, respectively, after they were spiked with calcium hypochlorite and the mean background of the unspiked sample was subtracted.

For the MC method, Figure 39 summarizes total chlorine standard deviation against mean total chlorine for spiked condenser water (Table 23, Experiments 23.3, 23.5, 23.7, 23.9, and 23.11), and Figure 40 summarizes relative standard deviation against mean total chlorine concentration. Figures 41-42 similarly summarize the statistical data for the AT method.

For the MC method, the results shown in Table 23 for spiked condenser cooling water from the Shawnee Steam Plant yield a total chlorine pooled standard deviation of 1.6 μg/l and mean relative standard deviation of 13.8 percent for concentrations of 2-20 μg/l chlorine (Experiment 23.3) and a total chlorine pooled standard deviation of 7.9 μg/l and a mean relative standard deviation of 11.5 percent for concentrations of 20-200 μg/l chlorine (Experiments 23.5, 23.7, and 23.9).

For the AT method, the results shown in Table 23 yield a total chlorine pooled standard deviation of 9.7 μg/l and a mean relative standard deviation of 28.8 percent (Experiments 23.3, 23.5, 23.7, and 23.9) for concentrations of 20-200 μg/l chlorine. These values are somewhat higher than those for the MC method (7.9 μg/l and 11.9 percent, respectively), the reverse of what was found for spiked condenser water from Kingston Steam Plant.

The MNDL of the MC method could not be calculated, because the mean recovery of 11.4 μg/l chlorine, the lowest recovery from spiked condenser water at the Shawnee Steam Plant (Experiment 23.3), was above the UCL for the MNDL. However, three valid MNDL values can be calculated for the AT method from recoveries shown by Experiments 23.3, 23.5, and 23.7. The MNDL values are 38.3, 26.7, and 29.9 μg/l for mean recoveries of 27.1, 21.4, and 47.1 μg/l, respectively. These values can be pooled to yield a valid pooled MNDL of 26.0 μg/l and a pooled mean recovery of 31.9 μg/l.

Precision and Minimum Detection Limit for Unspiked, Chlorinated Allen Steam Plant Water Samples

Table 24 shows the chlorine demand characteristics of unchlorinated river water used for condenser cooling at Allen Steam Plant chlorinated at particular concentrations for specified periods of time, and Table 25 shows its concentrations of inorganic species, sanitary chemical characteristics, and physical properties. The iron concentration of 1600 μg/l (Table 25) can be eliminated as a possible source of interference, as explained for the Kingston and Shawnee water samples. However, the sample from Allen Steam Plant contained 0.45 mg/l of ammonia as nitrogen (Table 25), whereas the samples from Kingston (Table 18) and Shawnee (Table 21) did not contain more than 0.06 mg/l. The chlorine demand for the Allen sample was also greater, and this was probably caused by the presence of ammonia.

Table 26, Experiments 26.1, 26.2, 26.4, 26.6, 26.8, and 26.10, shows recoveries by the MC and AT methods for seven replicate determinations of total chlorine in a series of six split samples of unspiked, chlorinated condenser cooling river water from Allen Steam Plant with total chlorine concentrations of 0-250 μg/l. The specific composition of each unspiked, chlorinated sample is given in Table 25.

For the MC method, Figure 43 summarizes total chlorine standard deviation against mean total chlorine in values from Table 26, Experiments 26.2, 26.4, 26.6, 26.8, and 26.10, and Figure 44 summarizes relative standard deviation against mean total chlorine. Figures 45-46 similarly the statistical results for the AT method.

The results obtained by the MC method in Experiment 26.10 were about 40 percent higher than those obtained by the AT method (mean recoveries of 247 and 177 µg/l, respectively). When 2 percent (w/v) sodium pyrophosphate decahydrate was added to the unspiked sample (Experiment 26.11) and the spiked sample (Experiment 26.12), there was closer agreement between the two methods; the mean recoveries by the MC method were only about 10 and 20 percent higher than those by the AT method for these respective samples. The high results obtained by the MC method may have been caused by the 0.45 mg/l of ammonia as nitrogen in the unchlorinated sample (Table 25) that continued to react with free chlorine to form combined chlorine (25) in the freshly composited sample on October 28, 1980, and by the fact that the MC method uses standard addition with chloramine-T (a combined source of chlorine) to assay for total chlorine, whereas the AT method uses direct titration with standard PAO. The large discrepancy between methods was absent on the following day, October 29, 1980, for unspiked samples composed of the same chlorinated and unchlorinated water, after its chlorine reactions had equilibrated for about a day and after the sample had probably lost most of its free chlorine, the only oxidant in the sample known to react with ammonia. Except in Experiment 26.7, however, no large discrepancy was observed for samples spiked with calcium hypochlorite on October 29, 1980. Since the same water sample was analyzed both days, this automatically eliminates the 1600 µg/l of iron and 670 µg/l of manganese in the sample (see Table 25) as possible sources for the high results. Furthermore, the MC method did not produce high results for chlorinated river water or for chlorinated condenser river water from Kingston, Shawnee, and John Sevier Steam Plants, probably because the ammonia was less than 0.06 mg/l as nitrogen (see results in Tables 14, 18, 21, and 28).

For the MC method, the experimental recoveries of total chlorine from unspiked, chlorinated condenser cooling river water from Allen Steam Plant (Table 26) yield a total chlorine pooled standard deviation of 7.4 µg/l and a mean relative standard deviation of 11.4 percent for concentrations of 20-200 µg/l chlorine (Experiments 26.2, 26.4, 26.6, and 26.8). These values approximate those for unspiked condenser water from the Shawnee and Kingston Steam Plants. No total chlorine data were obtained by the MC method for concentrations of 2-20 µg/l.

For the AT method, the results in Table 26 yield a total chlorine pooled standard deviation of 10.0 µg/l and a mean relative standard deviation of 15.4 percent (Experiments 26.2, 26.4, 26.6, 26.8, and 26.10) for concentrations of 20-200 µg/l chlorine. As with unspiked condenser water from Kingston and Shawnee, these values are slightly greater than those obtained by the MC method (7.4 µg/l and 11.4 percent, respectively).

The MNDL for the MC method is 10.1 μg/l chlorine for the mean recovery of 21.1 μg/l from unspiked, chlorinated condenser river water at Allen Steam Plant (Experiment 26.2). The MNDL for the AT method is 26.7 μg/l for the mean recovery of 21.1 μg/l shown in Experiment 26.2. The MNDL for the AT method obtained from unspiked sample results at Allen Steam Plant is similar to that for Kingston and Shawnee. Although no MNDL was obtained for the MC method for Shawnee, the one for Allen (10.1 μg/l) was several times higher than that for Kingston (2.0 μg/l).

A t value can be calculated from the split sample data obtained by the MC and AT methods for concentrations of 20-200 μg/l shown in Table 26, Experiments 26.2 (replicate numbers 2 and 4-7), 26.4, 26.6, and 26.8. Because the calculated t of 0.596 is less than that of 2.060 for $t_{0.025}$ with 25 degrees of freedom, there is no reason to conclude the mean of the differences between the MC and AT methods differs from zero at 95 percent significance. Also, the mean difference was 1.0 μg/l with standard deviation of 8.9 μg/l.

Precision and Minimum Detection Limit for Spiked, Chlorinated Allen Steam Plant Water Samples

Table 26, Experiments 26.3, 26.5, 26.7, 26.9, and 26.12, gives the total chlorine recoveries from the chlorinated Allen Steam Plant samples, shown in Experiments 26.2, 26.4, 26.6, 26.8, and 26.10, respectively, after they were spiked with calcium hypochlorite and the mean background of the unspiked sample was subtracted.

For the MC method, Figure 47 summarizes total chlorine standard deviation against mean total chlorine for spiked condenser water (Table 26, Experiments 26.3, 26.5, 26.7, 26.9, and 26.12), and Figure 48 summarizes relative standard deviation against mean total chlorine. Figures 49-50 similarly summarize the statistical results for the AT method.

For the MC method, the results shown in Table 26 for spiked condenser cooling water from the Allen Steam Plant yield, a total chlorine pooled standard deviation of 3.7 μg/l and a mean relative standard deviation of 19.5 percent for concentrations of 2-20 μg/l chlorine (Experiment 26.3) and a total chlorine pooled standard deviation of 8.9 μg/l and mean relative standard deviation of 12.7 percent for concentrations of 20-200 μg/l chlorine (Experiments 26.5, 26.7, 26.9, and 26.12).

For the AT method, the results in Table 26 yield a total chlorine pooled standard deviation of 14.6 μg/l and a mean relative standard deviation of 21.4 percent (Experiments 26.5, 26.7, 26.9, and 26.12) for concentrations of 20-200 μg.l. These values are nearly twice as large as those for the MC method (8.9 μg/l and 12.7 percent, respectively).

A pooled MNDL of 17.2 μg/l for a pooled mean recovery of 23.6 μg/l can be calculated for the MC method from the individually computed values of

11.6 and 25.8 μg/l with mean recoveries [illegible].0 and 28.3 μg/l, respectively, for spiked condenser water at Allen Steam Plant (Experiments 26.3 and 26.5). No valid MNDL values were calculated from spiked condenser water for the Kingston and Shawnee Steam P[illegible]

For the AT method, two MN[illegible] be calculated from the recoveries shown in Experiments 26.5 a[illegible] These MNDL values are 22.9 and 29.2 μg/l for mean recoveries of 3[illegible] and 25.7 μg/l, respectively. These values can be pooled to yield a valid pooled MNDL of 22.5 μg/l which has a pooled mean recovery of 30.0 μg/l. This pooled MNDL value compares well with the values of 26.0 and 31.9 μg/l obtained for spiked condenser water at Shawnee Steam Plant.

Precision and Minimum Detection Limit For Unspiked, Chlorinated John Sevier Steam Plant Water Samples

Table 27 shows the chlorine demand characteristics of unchlorinated river water used for condenser cooling at John Sevier Steam Plant chlorinated at particular concentrations for specified periods of time, and Table 28 shows its concentrations of inorganic species, sanitary chemical characteristics, and physical properties. None of the inorganic species shown in Table 28 were present in sufficiently high concentration to cause interference.

Table 29, Experiments 29.1, 29.2, 29.4, 29.6, 29.8, 29.10, and 29.12, shows recoveries by the MC and AT methods for seven replicate determinations of total chlorine from a series of seven split samples of unspiked, chlorinated condenser cooling river water from Allen Steam Plant with 0-325 μg/l total chlorine. The specific composition of the unspiked samples is given in Table 28.

For the MC method, Figure 51 summarizes total chlorine standard deviation against mean total chlorine for values from Table 29, Experiments 29.1, 29.2, 29.4, 29.6, 29.8, 29.10, and 29.12, and Figure 52 summarizes relative standard deviation against mean total chlorine. Figures 53-54 similarly summarize the statistical results for the AT method.

For the MC method, experimental recoveries of total chlorine from unspiked, chlorinated condenser cooling river water from John Sevier Steam Plant (Table 29) yield, a total chlorine pooled standard deviation of 0.5 μg/l and a mean relative standard deviation of 12.8 percent for concentrations of 2-20 μg/l (Experiments 29.1 and 29.2) and a total chlorine pooled standard deviation of 4.4 μg/l and a mean relative standard deviation of 7.5 percent for concentrations of 20-200 μg/l chlorine (Experiments 29.4, 29.6, 29.8, and 29.10). These values for total chlorine pooled standard deviation and mean relative standard deviation for John Sevier are similar to those for the MC method for concentrations of 20-200 μg/l chlorine in unspiked condenser water from Kingston and Allen Steam Plants (9.2 μg/l and 10.1 percent, 7.9 μg/l and 6.8 pecent, and 7.4 μg/l and 11.4 percent, respectively). For the MC method, the total chlorine standard deviation of 0.5 μg/l and mean relative standard deviation of 12.8 percent for concentrations of 2-20 μg/l chlorine in unspiked condenser water from John Sevier Steam Plant compare to total chlorine standard deviations of 1.0 and 4.5 μg/l and mean relative standard deviations of 8.8 and 56.9 percent for the Kingston and Shawnee Steam Plants, respectively. No comparable data were obtained at Allen Steam Plant.

For the AT method, results in Table 29 yield a total chlorine pooled standard deviation of 7.5 and a mean relative standard deviation of 11.8 percent (Experiments 29.4, 29.6, 29.8, and 29.10) for concentrations of 20-200 μg/l chlorine. As was the case for unspiked condenser cooling water at Kingston, Shawnee, and Allen, these values for the AT method are greater than those for the MC method (4.4 μg/l and 7.5 percent, respectively). The values for John Sevier compare to the 6.4, 9.9, and 10.0 μg/l total chlorine pooled standard deviation values and 9.5, 14.3, and 15.4 percent mean relative standard deviation values for the AT method for concentrations of 20-200 μg/l chlorine for unspiked condenser water at the Kingston, Shawnee, and Allen Steam Plants and to those of 4.9, 7.9, and 7.4 μg/l and 5.0, 6.8, and 11.4 percent, respectively, for the MC method for the same concentrations for the same steam plants.

For the MC method, MNDL values of 1.3 and 12.6 μg/l for mean recoveries of 2.10 and 25.9 μg/l can be calculated from the data shown in Experiments 29.1 and 29.4. These MNDL values could not be combined, because the pooled mean recovery of 14.0 μg/l was above the pooled UCL for the combined MNDL. For the AT method, the pooled MNDL is 16.6 μg/l for a pooled mean recovery of 22.1 μg/l (from data for Experiments 29.2 and 29.4). The individual MNDL values for the latter two experiments are 19.8 and 19.2 μg/l with mean recoveries of 13.5 and 30.7 μg/l, respectively.

For the MC method, MNDL values of 1.3 and 12.6 μg chlorine/l for unspiked condenser water at John Sevier Steam Plant compare with those of 2.0 and 10.1 μg/l for unspiked condenser water at the Kingston and Allen Steam Plants, respectively. No MNDL was obtained for the MC method for the Shawnee Steam Plant.

For the AT method, the pooled MNDL of 16.6 μg/l for unspiked condenser water at the John Sevier Steam Plant compares with that of 26.7, 22.0 or 25.5, and 23.6 μg/l for unspiked condenser water at Allen, Shawnee, and Kingston. For all steam plants, the MNDL for the AT method was higher than that for the MC method.

As was the case for the Kingston, Shawnee, and Allen results, a t value can be calculated from the split sample data obtained by the MC and AT methods for concentrations of 20-200 μg/l shown in Table 29, Experiments 29.2 (Replicate Numbers 1 and 7), 29.4, 29.6, 29.8, and 29.10. Because the absolute value of the calculated t of -0.779 is less than that of 2.045 for $t_{0.025}$ with 29 degrees of freedom, there is no reason to conclude the mean of the differences between the MC and AT methods differs from zero at 95 percent significance. Also, the mean differences was -1.6 μg/l with standard deviation of 10.9 μg/l.

Precision and Minimum Detection Limit for Spiked, Chlorinated John Sevier Steam Plant Water Samples

Table 29, Experiments 29.3, 29.5, 29.7, 29.9, 29.11, and 29.13, shows the total chlorine recoveries from the chlorinated John Sevier Steam Plant samples (Experiments 29.2, 29.4, 29.6, 29.8, 29.10, and 29.12, respectively), after they had been spiked with calcium hypochlorite and the mean background of the unspiked sample had been subtracted.

For the MC method, Figure 55 summarizes total chlorine standard deviation against mean total chlorine for spiked condenser water (Table 29, Experiments 29.3, 29.5, 29.7, 29.9, 29.11, and 29.13), and Figure 56 summarizes relative standard deviation against mean total chlorine. Figures 57 and 58 similarly summarizes the statistical results for the AT method.

For the MC method, experimental recoveries from spiked condenser cooling water from the John Sevier Steam Plant yield a total chlorine pooled standard deviation of 0.9 μg/l and mean relative standard deviation of 12.7 percent for concentrations of 2-20 μg/l chlorine (Experiments 29.3 and 29.5) and a total chlorine pooled standard deviation of 8.6 μg/l and mean relative standard deviation of 7.7 percent for concentrations of 20-200 μg/l chlorine (Experiments 29.7, 29.9, 29.11, and 29.13).

For the AT method, the results in Table 29 yield a total chlorine pooled standard deviation of 9.0 μg/l and a mean relative standard deviation of 20.4 percent (Experiments 29.5, 29.7, 29.9, and 29.11) for concentrations of 20-200 μg/l chlorine. These values for the AT method are higher than those for the MC method for the same spiked water from the same plant (8.6 μg/l and 7.7 percent, respectively). These values compare to the 5.5, 9.7, and 14.6 μg/l total chlorine pooled standard deviation values and 7.8, 28.8, and 21.4 percent mean relative standard deviation values for the AT method and to those of 9.2, 7.9, and 8.9 μg/l and 10.1, 11.5, and 12.7 percent, respectively, for the MC method for concentrations of 20-200 μg/l chlorine for spiked condenser water at the Kingston, Shawnee, and Allen Steam Plants.

The MNDL for the MC method for spiked condenser water at John Sevier Steam Plant is 3.2 μg/l for a mean recovery of 5.11 μg/l (Experiment 29.3). For the AT method, the pooled MNDL is 23.1 μg/l for a pooled mean recovery of 29.2 μg/l (from data from Experiments 29.5 and 29.7). The individual MNDL values for the latter two experiments are 23.6 and 29.9 μg/l with mean recoveries of 21.4 and 37.1 μg/l, respectively.

The MNDL of 3.2 μg/l for the MC method for spiked condenser water at John Sevier Steam Plant is considerably less than the pooled MNDL of 17.2 μg/l for spiked condenser water at Allen, the only water with an appreciable concentration of ammonia (Table 25). No valid MNDL values could be estimated for the MC method from data gathered for spiked condenser water at the Kingston and Shawnee Plants.

For the AT method, the pooled MNDL of 23.1 μg/l for spiked condenser water at the John Sevier Steam Plant is about the same as the pooled MNDL of 26.0 μg/l for spiked condenser water at the Shawnee Steam Plant and the pooled MNDL of 22.5 μg/l for spiked water at Allen. A valid MNDL could not be derived from data for spiked water at Kingston.

Overall Precision and Minimum Detection Limit for Unspiked, Chlorinated Kingston, Shawnee, Allen, and John Sevier Steam Plant Water Samples

The pooled standard deviations and mean relative standard deviations for the MC and AT methods for the recovery experiments with unspiked, chlorinated condenser cooling river water samples from the Kingston, Shawnee, Allen, and John Sevier Steam Plants can be combined to yield the overall values.

For the MC method, the total chlorine overall pooled standard deviation and the overall mean relative standard deviation are 2.1 μg/l and 20.8 percent, respectively, for concentrations of 2-20 μg/l chlorine (Table 19, Experiments 19.1 and 19.2; Table 23, Experiment 23.2; Table 29, Experiments 29.1 and 29.2) and the total chlorine overall pooled standard deviation and the overall mean relative standard deviation are 6.3 μg/l and 7.7 percent for concentrations of 20-200 μg/l chlorine (Table 19, Experiments 19.4, 19.6, 19.8, and 19.10; Table 23, Experiments 23.4, 23.6, 23.8, and 23.10; Table 26, Experiments 26.2, 26.4, 26.6, and 26.8; Table 29, Experiments 29.4, 29.6, 29.8, and 29.10). For the MC method, the total chlorine overall pooled standard deviation (2.1 μg/l) and overall mean relative standard deviation (20.8 percent) for concentrations of 2-20 μg/l chlorine in unspiked condenser water are greater than the respective values for the same range of concentrations in spiked river water (0.5 μg/l and 4.8 percent) or in spiked deionized water (0.5 μg/l and 8.7 percent). For the MC method, the total chlorine overall pooled standard deviation (6.3 μg/l) and overall mean relative standard deviation (7.7 percent) for concentrations of 20-200 μg/l chlorine in unspiked condenser water are greater than the respective values for the same range of concentrations in spiked river water (2.3 μg/l and 2.4 percent) or in spiked deionized water (5.9 μg/l and 3.9 percent).

For the AT method, the total chlorine overall pooled standard deviation and overall mean relative standard deviation are 8.7 μg/l and 12.9 percent, respectively, for concentrations of 20-200 μg/l chlorine in unspiked, chlorinated condenser cooling river water (Table 19, Experiments 19.4, 19.6, 19.8, and 19.10; Table 23, Experiments 23.4, 23.6, 23.8, and 23.10; Table 26, Experiments 26.2, 26.4, 26.6, 26.8, and 26.10; Table 29, Experiments 29.4, 29.6, 29.8, and 29.10). For the AT method, the total chlorine overall pooled standard deviation (8.7 μg/l) and overall mean relative standard deviation (12.9 percent) for concentrations of 20-200 μg/l chlorine in unspiked condenser water are greater than the respective values for the same range of concentrations in spiked river water (3.9 μg/l and 6.3 percent) or in spiked deionized water (4.0 μg/l and 5.0 percent).

For concentrations of 20-200 μg/l chlorine in unspiked, chlorinated condenser cooling river water, the total chlorine overall pooled standard deviation of 6.3 μg/l and overall mean relative standard deviation of 7.7 percent for the MC method are lower than the total chlorine overall pooled standard deviation of 8.7 μg/l and overall mean relative standard deviation of 12.9 percent for the AT method. The total chlorine overall pooled standard deviation of 8.7 μg/l obtained in this study for the AT method for 20-200 μg/l in unspiked chlorinated condenser water is lower than the 28 μg/l obtained in a collaborative test study with unspiked, chlorinated condenser water for 0-200 μg/l (4). The collaborative test study (4) included sampling variation and operator-to-operator variation in addition to the instrumental, kind of sample, and single-operator variation involved in this study.

A valid overall pooled MNDL could not be calculated for the MC method by combining the individual valid MNDL values of 2.0 μg/l for unspiked, chlorinated condenser water from the Kingston Steam Plant, 10.1 μg/l from the Allen Plant; and 1.3 and 12.6 μg/l from the John Sevier Plant (Table 19, Experiment 19.1; Table 26, Experiment 26.2; Table 29, Experiments 29.1 and 29.4) because the mean for the combined results (13.3 μg/l) was greater than the UCL (9.03 μg/l) for the overall MNDL (6.5 μg/l). However, the invalid overall estimate of 6.5 μg/l for the MNDL as well as the individual valid MNDL values of 2.0, 10.1, 1.3, and 12.6 μg/l are greater than the valid MNDL of 1.2 μg/l for deionized water spiked with chloramine-T (Table 7, Experiment 7.3). For the MC method, Rigdon estimated an MNDL of 3 or 4 μg/l in deionized water spiked with chloramine-T (6,7).

Although not subjected to the validation test, the overall MNDL for the AT method is 17.8 μg/l for the combined results of individual valid MNDL values of 23.6 μg/l from the Kingston Steam Plant (Table 19, Experiment 19.6); 22.0 and 25.5 μg/l from the Shawnee Plant (Table 23, Experiments 23.4 and 23.6); 26.7 μg/l from the Allen Plant (Table 26, Experiment 26.2); and 19.8 and 19.2 μg/l from the John Sevier Plant (Table 29, Experiments 29.2 and 29.4). The overall MNDL of 17.8 μg/l is greater than the individual valid MNDL values of 11.9, 16.7, and 15.1 μg/l for river water spiked with chloramine-T (Table 15, Experiments 15.2, 15.4, and 15.5) and the valid overall pooled MNDL of 12.0 μg/l for deionized water spiked with calcium hypochlorite (Table 11, Experiments 11.3 and 11.4) and 50 percent (w/w) calcium hypochlorite and chloramine-T as chlorine (Table 12, Experiment 12.3).

For unspiked, chlorinated condenser water from the Kingston, Shawnee, Allen, and John Sevier Steam Plants, the overall MNDL of 6.5 μg/l for the MC method is lower than that of 17.8 μg/l for the AT method. The overall MNDL of 17.8 μg/l in unspiked condenser water, which was estimated in this study, is lower than the 85 μg/l obtained in a collaborative test study with unspiked, chlorinated condenser water (4). The collaborative test study (4) included sampling and operator-to-operator variation as well as the instrumental, kind of sample, and single-operator variation involved in this study.

A t value can be calculated from the split sample data for the MC and AT methods for concentrations of 20-200 µg/l for all split sample results for unspiked, chlorinated condenser water from Kingston, Shawnee, Allen, and John Sevier, shown in Table 19, Experiments 19.4, 19.6, 19.8, and 19.10; Table 23, Experiments 23.4, 23.6, 23.8, and 23.10; Table 26, Experiments 26.2 (Replicate Numbers 2 and 4-7), 26.4, 26.6, and 26.8; and Table 29, Experiments 29.2 (Replicate Numbers 1 and 7), 29.4, 29.6, 29.8, and 29.10. Because the absolute value of the calculated t of -0.091 is less than that of 1.96 with 111 degrees of freedom, there is no reason to conclude the mean of the differences between the MC and AT methods differs from zero at 95 percent significance. Also, the mean difference was -0.1 µg/l with standard deviation of 13.0 µg/l.

Overall Precision and Minimum Detection Limit for Spiked, Chlorinated Kingston, Shawnee, Allen, and John Sevier Steam Plant Water Samples

The pooled standard deviations and mean relative standard deviations for the MC and AT methods for the recovery experiments with the spiked, chlorinated condenser cooling river water samples from the Kingston, Shawnee, Allen, and John Sevier Steam Plants can be combined to yield overall values.

For the MC method, the total chlorine overall pooled standard deviation and the overall mean relative standard deviation are 1.9 µg/l and 13.5 percent, respectively, for concentrations of 2-20 µg/l chlorine (Table 19, Experiment 19.3; Table 23, Experiment 23.3; Table 26, Experiment 26.3; Table 29, Experiments 29.3 and 29.5); and the total chlorine overall pooled standard deviation and the overall mean relative standard deviation are 8.7 µg/l and 10.4 percent for concentrations of 20-200 µg/l chlorine (Table 19, Experiments 19.5, 19.7, 19.9, 19.11; Table 23, Experiments 23.5, 23.7, 23.9; Table 26, Experiments 26.5, 26.7, 26.9, 26.11; Table 29, Experiments 29.7, 29.9, 29.11, and 29.13). For the MC method, the total chlorine overall pooled standard deviations of 1.9 and 8.7 µg/l for concentrations of 2-20 and 20-200 µg/l chlorine, respectively, for spiked, chlorinated condenser water from the Kingston, Shawnee, Allen, and John Sevier Steam Plants can be compared with 2.1 and 6.3 µg/l for concentrations of 2-20 and 20-200 µg/l, respectively, for unspiked, chlorinated condenser water from the same four steam plants. For concentrations of 2-20 µg/l, the total chlorine overall standard deviations of 1.9 and 2.1 µg/l are similar for spiked and unspiked condenser water, but for concentrations of 20-200 µg/l, the total chlorine standard deviation of 8.7 µg/l for spiked condenser water is greater by approximately $\sqrt{2}$ than that of 6.3 µg/l for unspiked condenser water, which is the theoretical expected increase in the standard deviation derived from differences (26).

For the AT method, for concentrations of 20-200 μg/l in spiked, chlorinated condenser cooling river water, the total chlorine overall pooled standard deviation and overall mean relative standard deviation are 10.2 μg/l and 19.6 percent, respectively (Table 19, Experiments 19.5, 19.7, 19.9, 19.11; Table 23, Experiments 23.3, 23.5, 23.7, and 23.9; Table 26, Experiments 26.5, 26.7, 26.9, and 26.12; Table 29, Experiments 29.5, 29.7, 29.9, and 29.11). For concentrations of 20-200 μg/l chlorine, the total chlorine overall standard deviation of 10.2 μg/l for the AT method for spiked, chlorinated condenser water from the Kingston, Shawnee, Allen, and John Sevier Steam Plants is greater than that of 8.7 μg/l for unspiked, chlorinated condenser water from the same four steam plants. It is not greater by $\sqrt{2}$, which would be expected ideally (26).

For concentrations of 20-200 μg/l in spiked, chlorinated condenser cooling river water, the total chlorine overall pooled standard deviation of 8.7 μg/l and overall mean relative standard deviation of 10.4 percent for the MC method is lower than the total chlorine overall pooled standard deviation of 10.2 μg/l and overall mean relative standard deviation of 19.6 percent for the AT method.

Although not subjected to the validation test, the overall MNDL of the MC method for spiked, chlorinated condenser water is 13.3 μg/l for the combined results of individual valid MNDL values of 11.6 and 25.8 μg/l from Allen Steam Plant (Table 26, Experiments 26.3 and 26.5) and 3.2 μg/l from the John Sevier Plant (Table 29, Experiment 29.3). This MNDL value of 13.3 μg/l for the MC method for spiked condenser water is about twice that of 6.5 μg/l for unspiked condenser water, for which the associated individual MNDL values are 2.0, 10.1, 1.3, and 12.6 μg/l.

Although not subjected to the validation test, the overall MNDL for the AT method is 22.2 μg/l for spiked condenser water, for which the individual valid MNDL values are 38.3, 26.7, and 29.9 μg/l for Shawnee Steam Plant (Table 23, Experiments 23.3, 23.5, and 23.7); 22.9 and 29.2 μg/l for Allen Plant (Table 28, Experiments 26.5 and 26.7); and 23.6 and 29.9 μg/l for the John Sevier Steam Plant (Table 29, Experiments 29.5 and 29.7). This value of 22.2 μg/l for the AT method for spiked condenser water is larger than that of 17.8 μg/l for unspiked condenser water, for which the associated individual valid MNDL values are 23.6, 22.0, 25.5, 26.7, 19.8, and 19.2 μg/l.

For spiked, chlorinated condenser water from Kingston, Shawnee, Allen, and John Sevier Steam Plants, the overall MNDL of 13.3 μg/l for the MC method is lower than that of 22.2 μg/l for the AT method.

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GLOSSARY

free chlorine (FC): Also known as free available chlorine. When chlorine reacts with water, hypochlorous acid and hydrochloric acid are formed:

$$Cl_2 + H_2O \rightarrow \underset{\text{hypochlorus acid}}{HOCl} + \underset{\text{hydrochloric acid}}{HCl}$$

The hypochlorous acid further dissociates into hypochlorite ion and hydrogen ion.

$$HOCl \rightarrow OCl^- + H^+$$

FC is the sum of the HOCl and OCl^- fractions in the chlorinated solutions.

combined chlorine (CC): When HOCl combines with ammonia in the water, mono-, di-, and trichloramine are formed. The sum of these three fractions is called combined chlorine.

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$$

monochloramine

$$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$$

dichloramine

$$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$$

trichloramine

total chlorine (TC): The sum of the FC and CC and fractions.

chlorine demand: The difference between the amount of chlorine added to the water and the amount of TC remaining at the end of a specified contact period.

chloramine-T: Chloramine-T trihydrate. Also known as sodium N-chloro-p-toluenesulfonamide trihydrate.

gran function (Gi) and volume addition (i): These terms are defined in reference 7.

mean, standard deviation (SD), and relative standard deviation (RSD): These terms are defined in reference 18.

% bias: Also known as percentage accuracy, which is defined in reference 18.

maximum detection limit: A subjective judgment of the highest concentration that can be determined with useful accuracy and precision for the intended application of the analytical method.

minimum detection limit: A subjective judgment of the lowest concentration that can be determined with useful accuracy and precision for the intended application of the analytical method.

pH: Negative logarithm of hydrogen ion concentration.

steam plant: Coal-burning electric power plant.

Figures

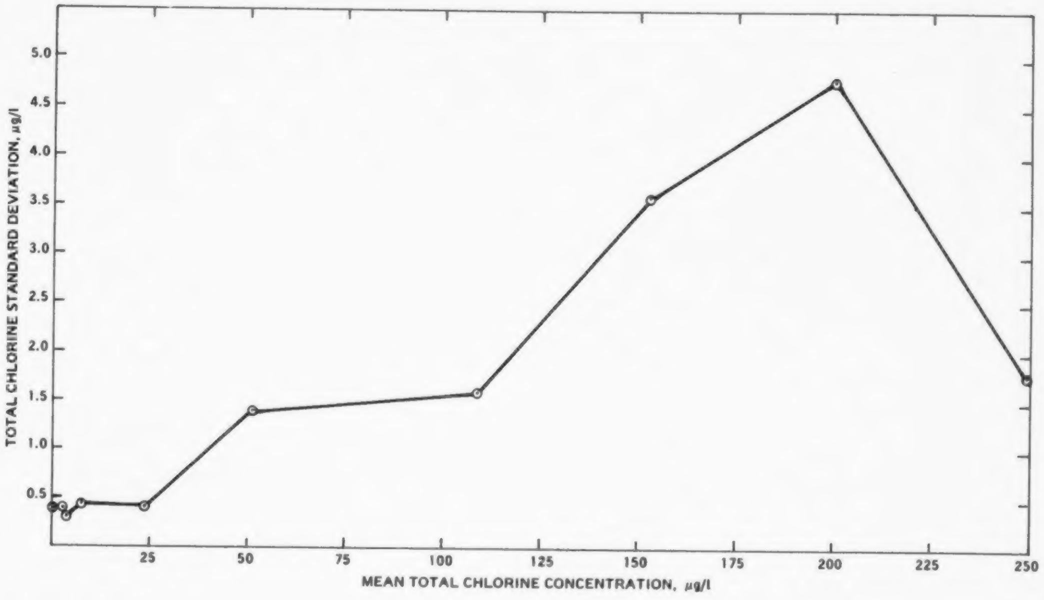

Figure 1. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from deionized water spiked with chloramine-T.

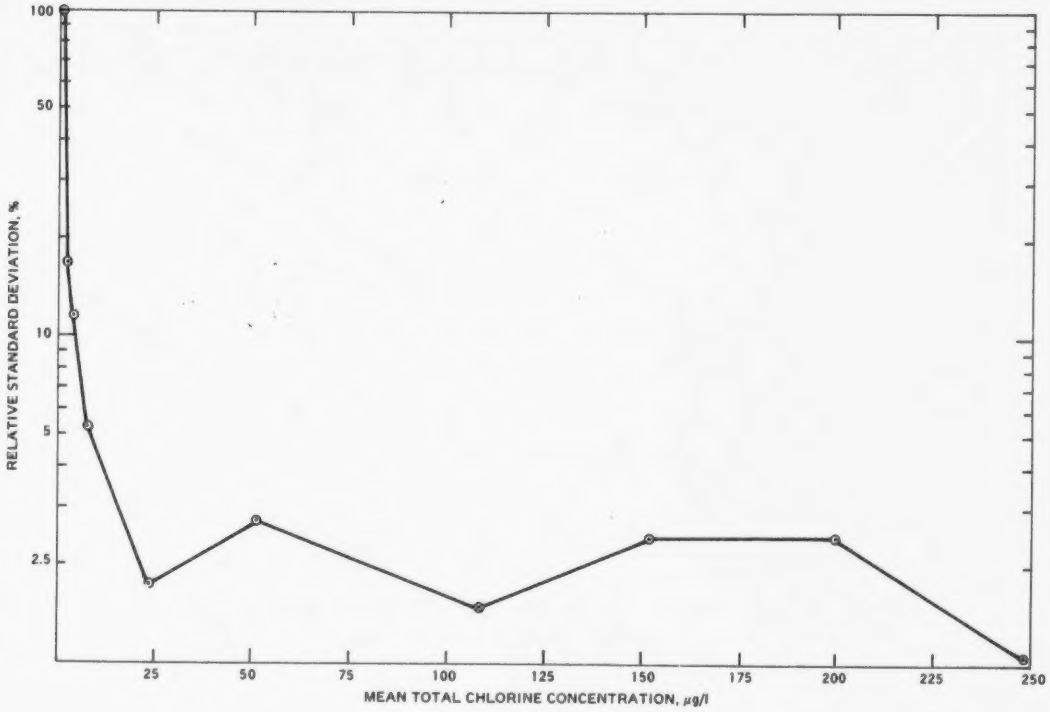

Figure 2. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from deionized water spiked with chloramine-T.

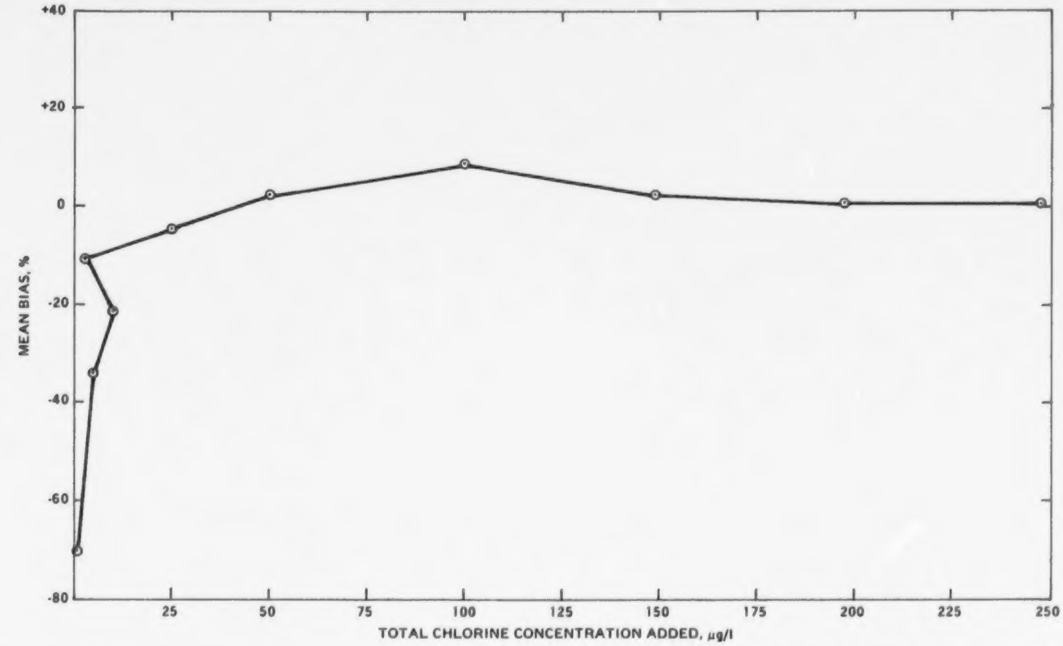

Figure 3. Percentage mean bias against total chlorine concentration added in micrograms per liter for experimental recovery by MC method of total chlorine from deionized water spiked with chloramine-T.

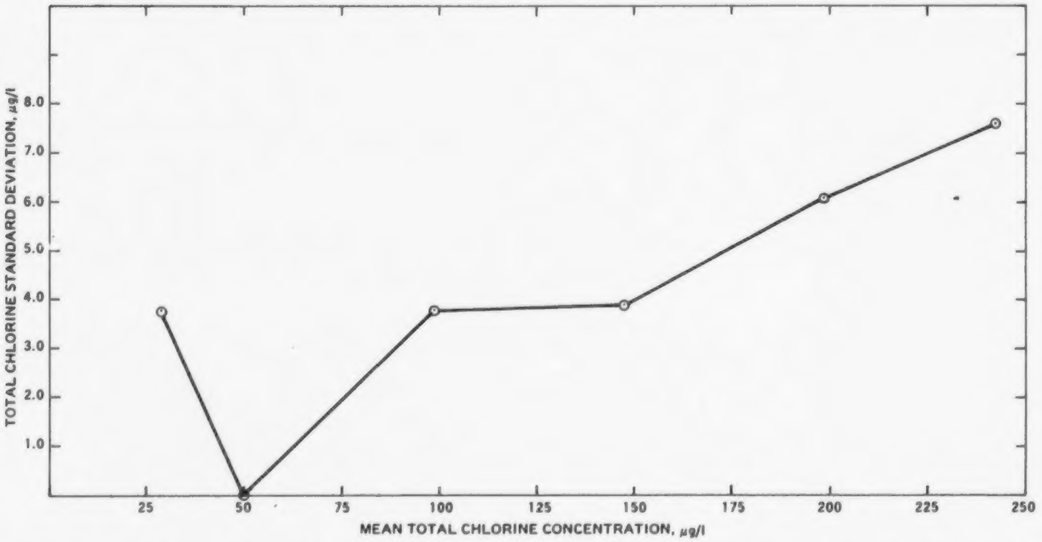

Figure 4. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from deionized water spiked with chloramine-T.

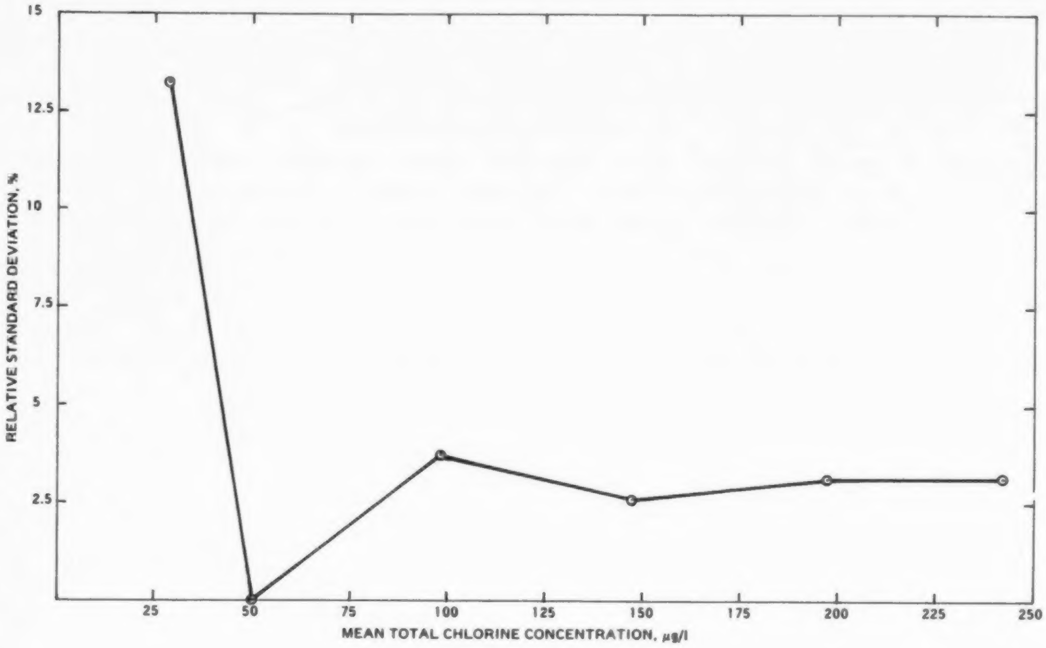

Figure 5. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from deionized water spiked with chloramine-T.

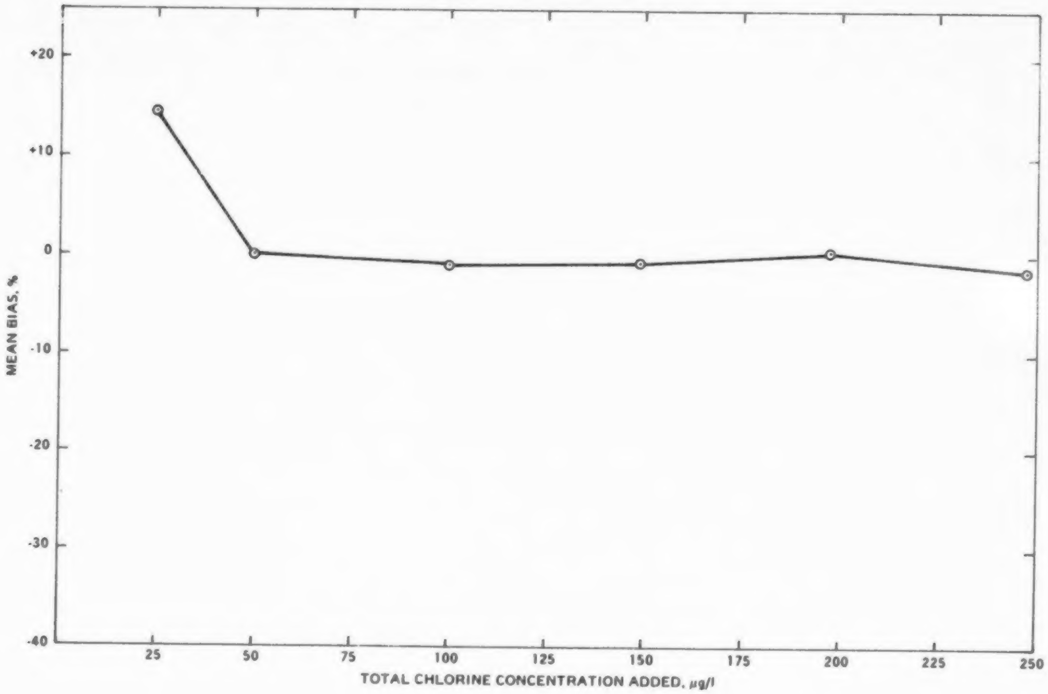

Figure 6. Percentage mean bias against total chlorine concentration added in micrograms per liter for experimental recovery by AT method of total chlorine from deionized water spiked with chloramine-T.

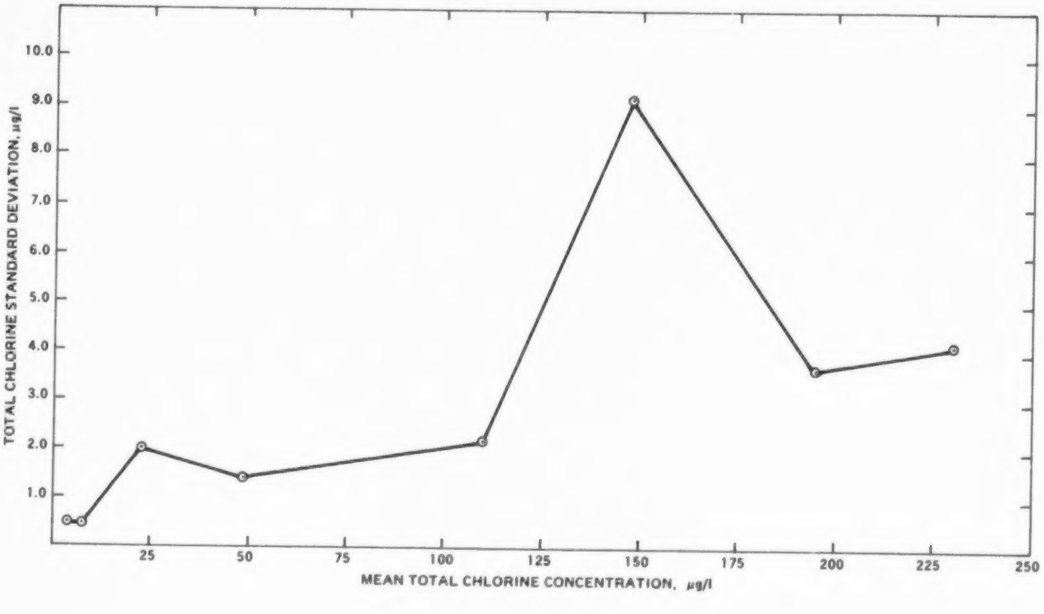

Figure 7. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from deionized water spiked with calcium hypochlorite.

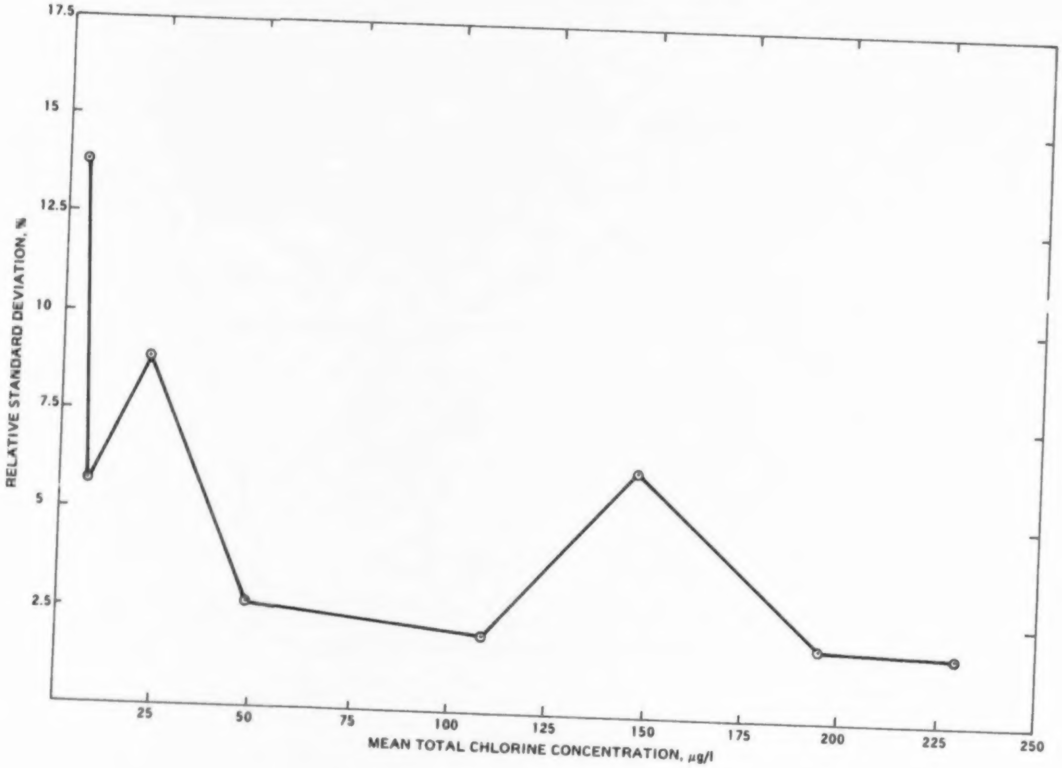

Figure 8. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from deionized water spiked with calcium hypochlorite.

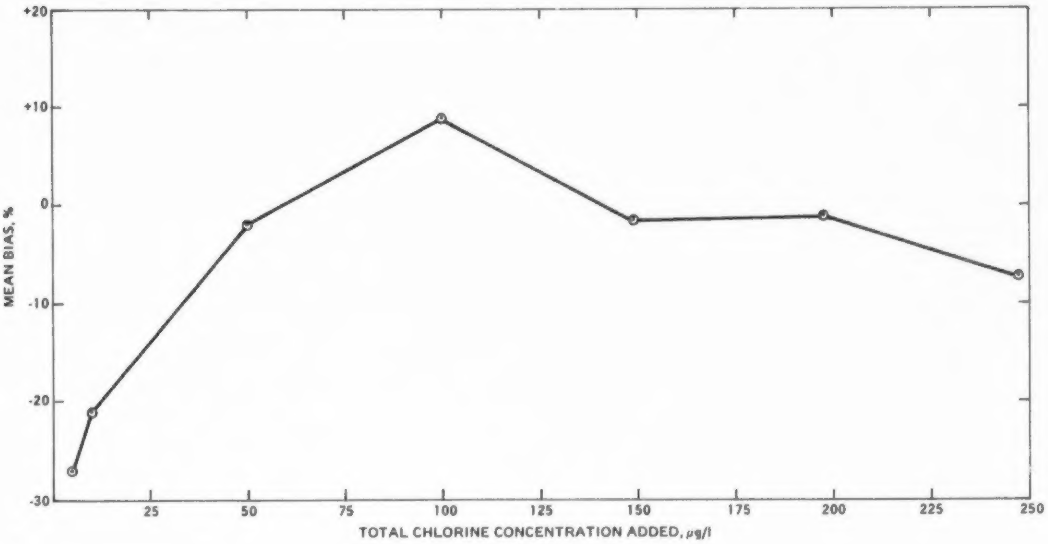

Figure 9. Percentage mean bias against total chlorine concentration added in micrograms per liter for experimental recovery by MC method of total chlorine from deionized water spiked with calcium hypochlorite.

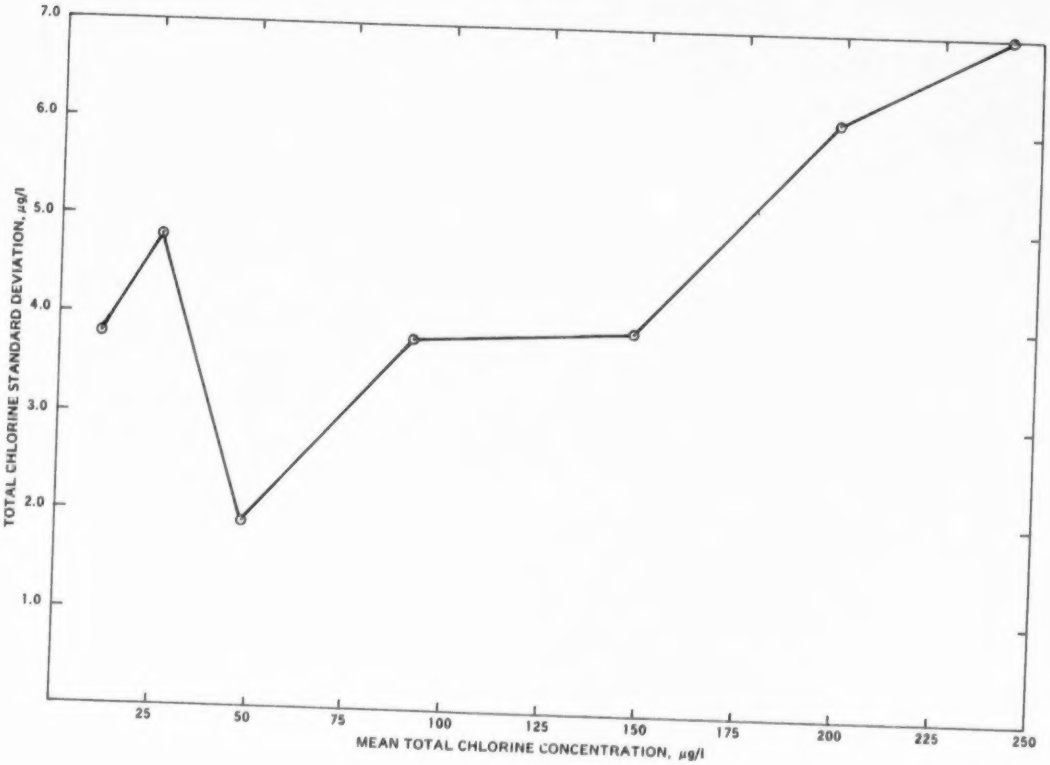

Figure 10. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from deionized water spiked with calcium hypochlorite.

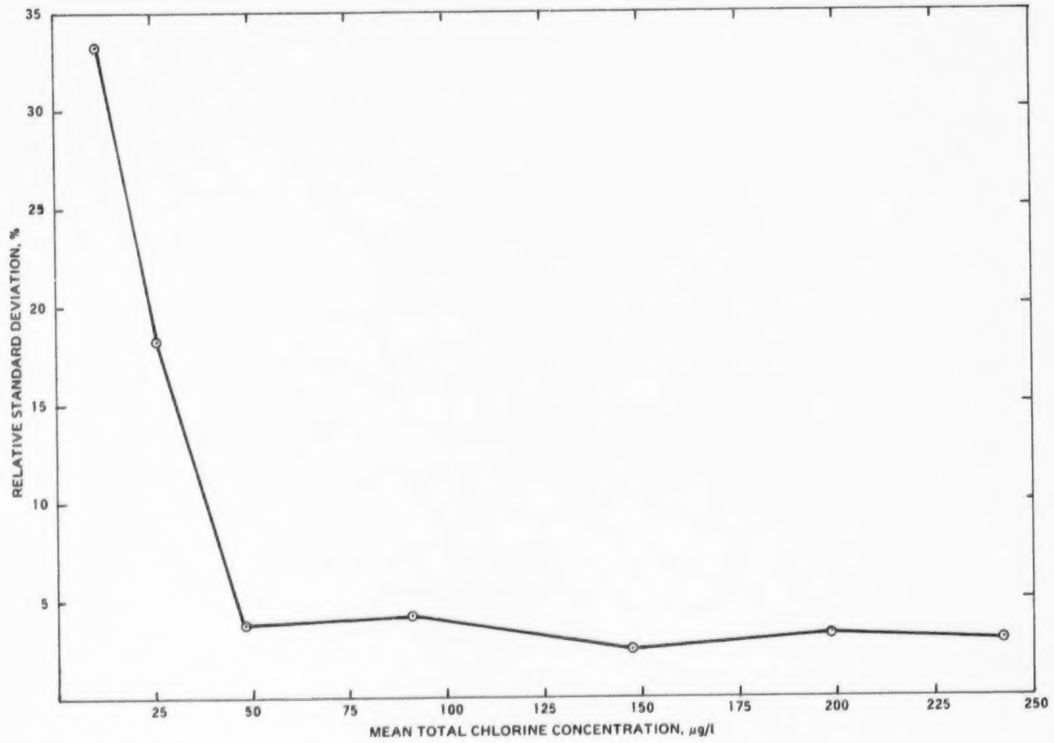

Figure 11. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from deionized water spiked with calcium hypochlorite.

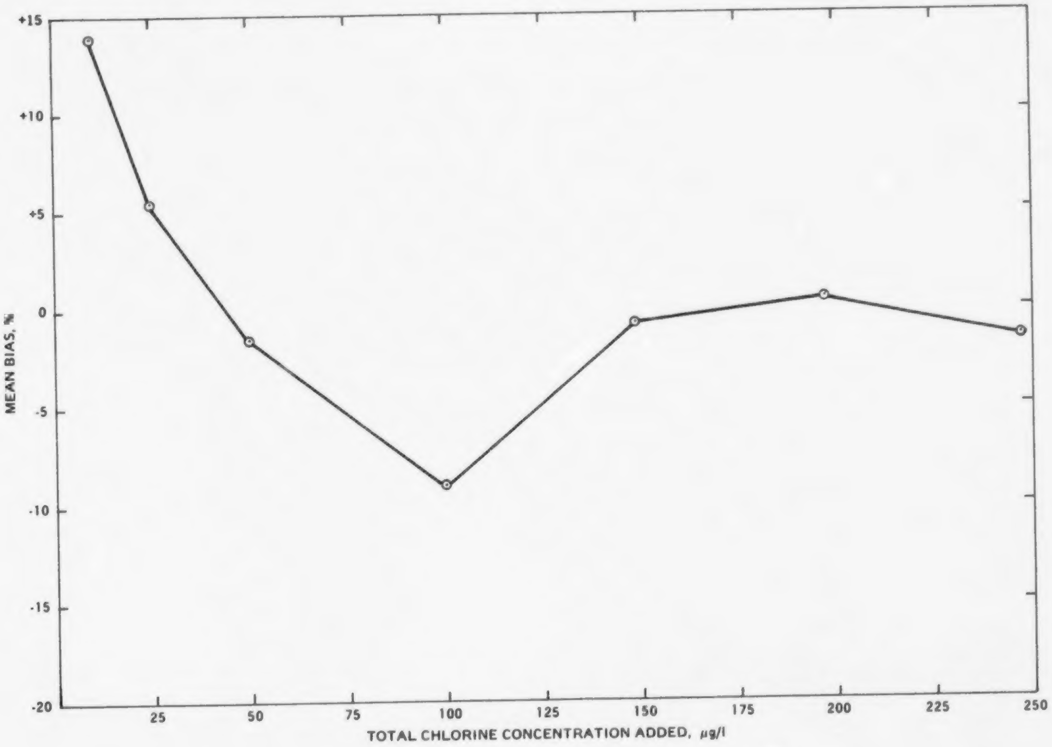

Figure 12. Percentage mean bias against total chlorine concentration added in micrograms per liter for experimental recovery by AT method of total chlorine from deionized water spiked with calcium hypochlorite.

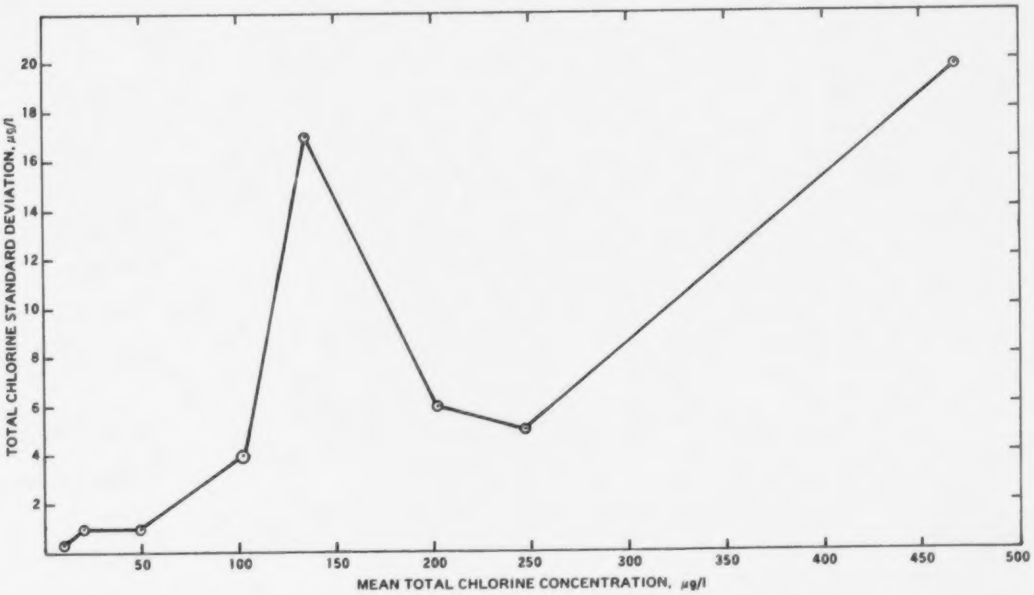

Figure 13. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from deionized water spiked with 50% (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine.

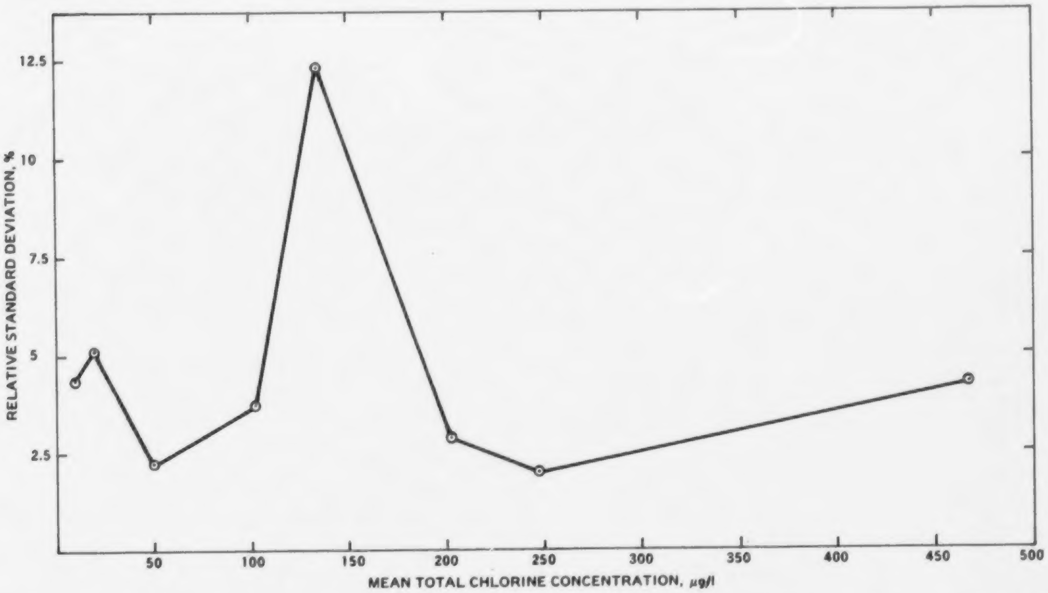

Figure 14. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from deionized water spiked with 50% (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine.

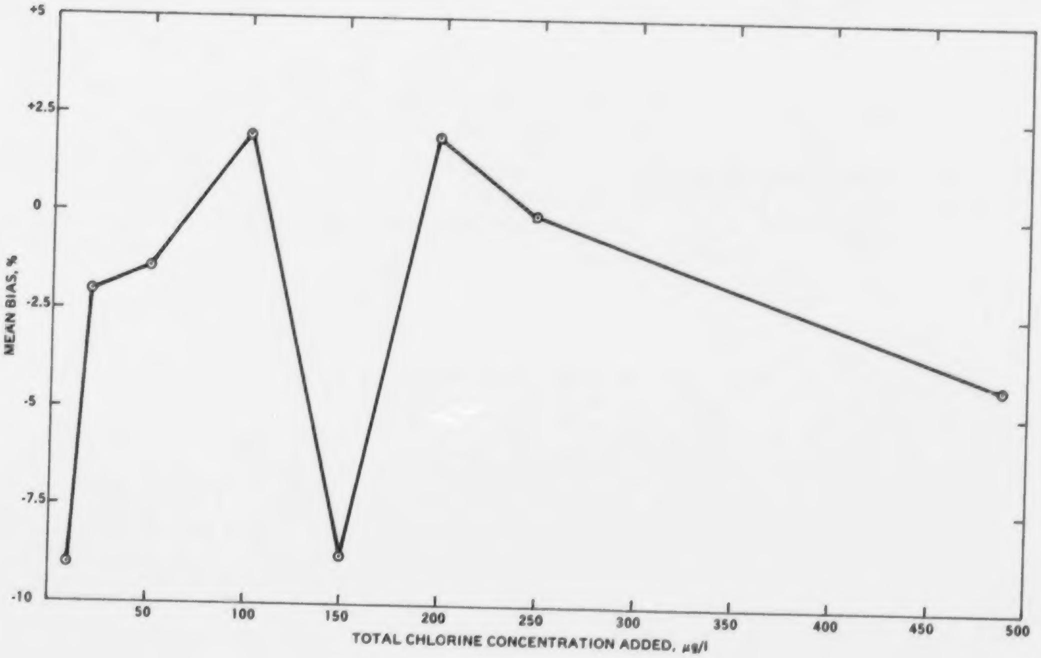

Figure 15. Percentage mean bias against total chlorine concentration added in micrograms per liter for experimental recovery by MC method of total chlorine from deionized water spiked with 50% (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine.

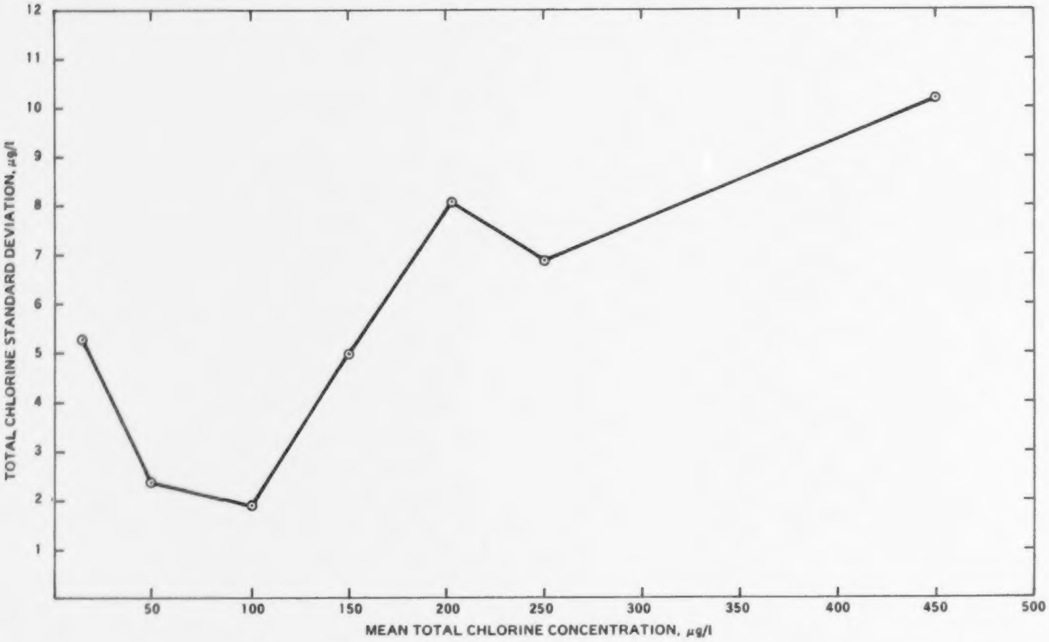

Figure 16. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration for experimental recovery by AT method of total chlorine from deionized water spiked with 50% (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine.

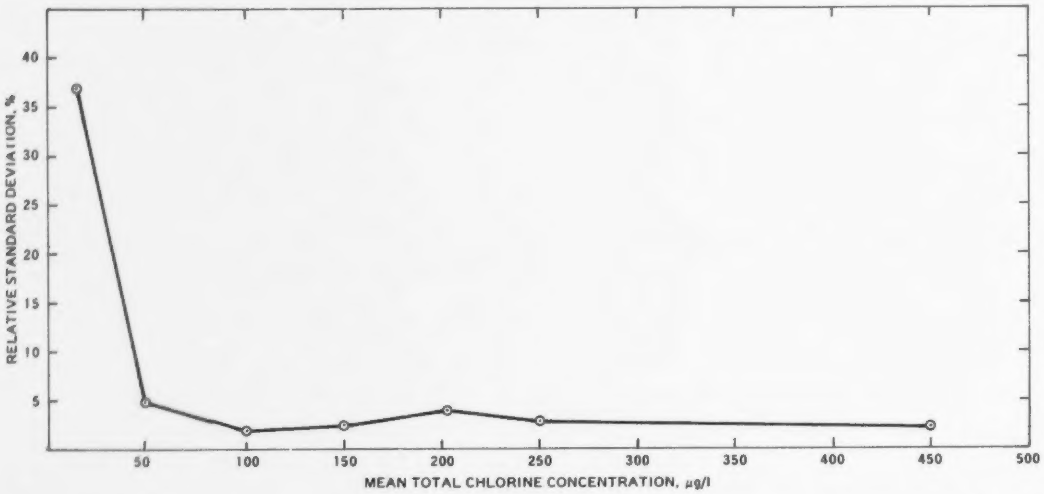

Figure 17. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from deionized water spiked with 50% (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine.

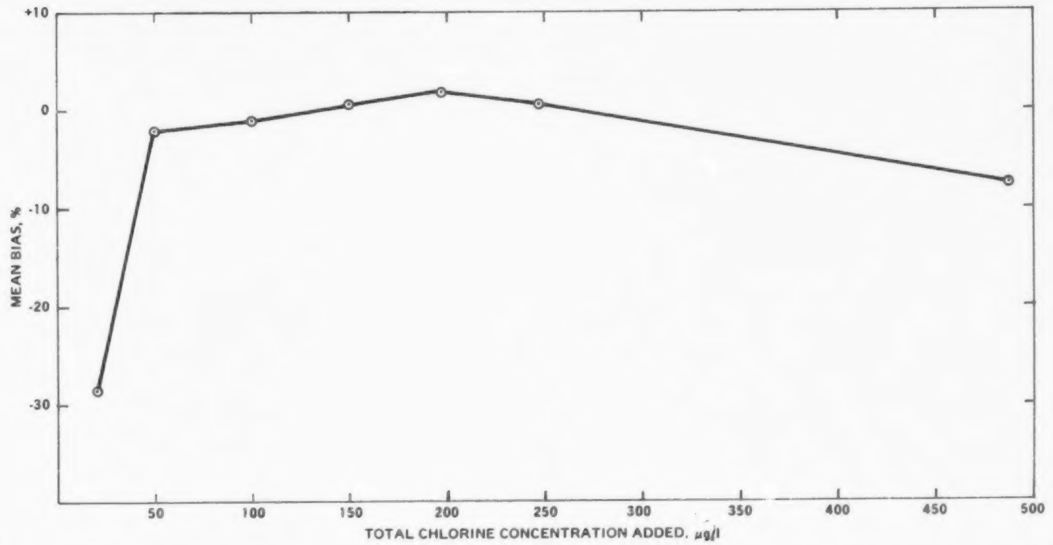

Figure 18. Percentage mean bias against total chlorine concentration added in micrograms per liter for experimental recovery by AT method of total chlorine from deionized water spiked with 50% (w/w) mixture of calcium hypochlorite and chloramine-T as chlorine.

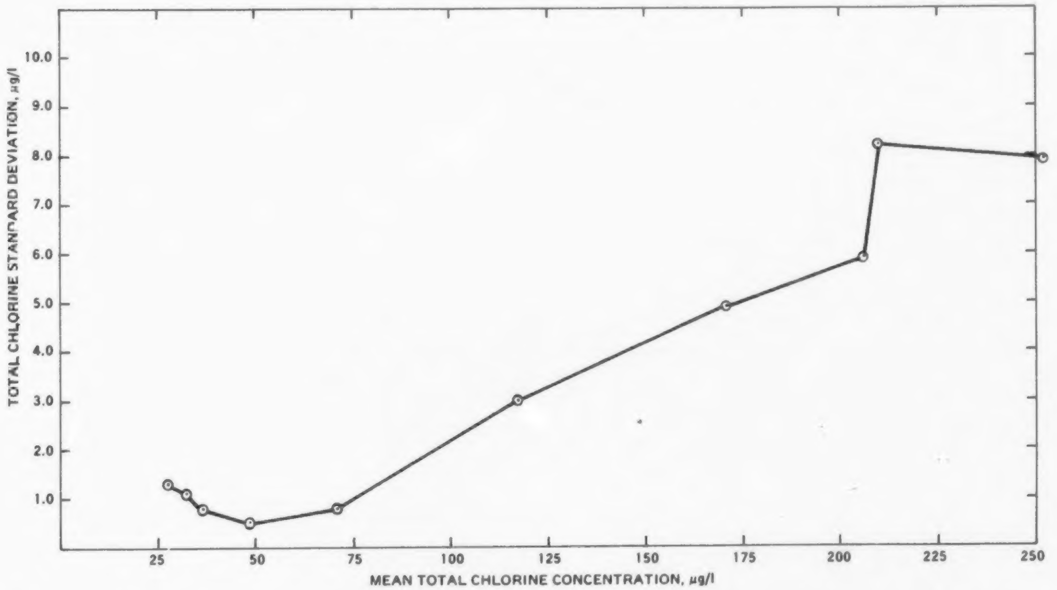

Figure 19. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw Ross Landing surface river water sample collected October 3, 1980, analyzed October 7-12, 1980, spiked with chloramine-T.

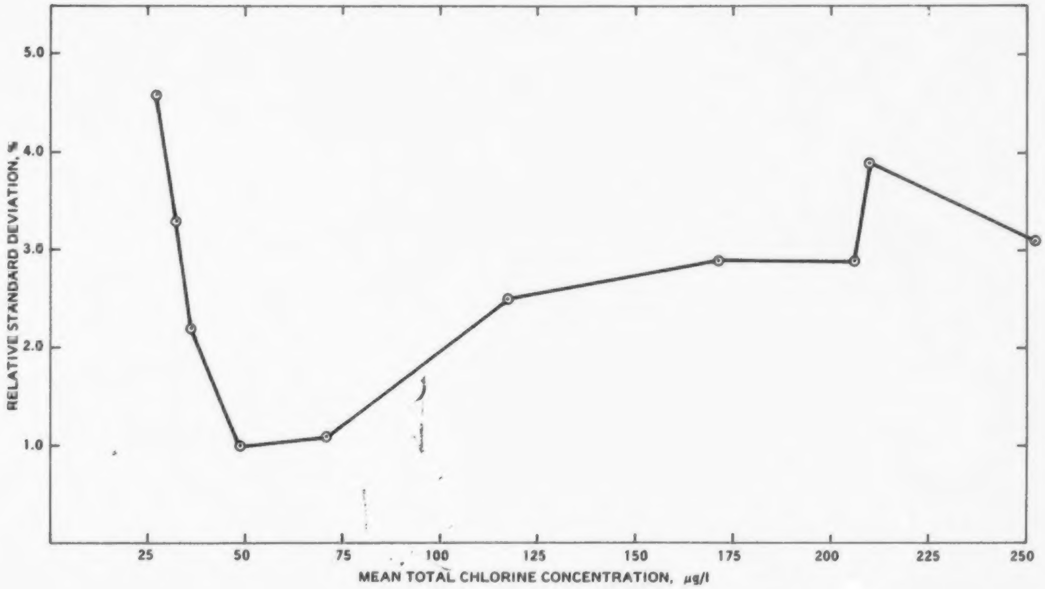

Figure 20. Percentage relative standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw Ross Landing surface river water sample collected October 3, 1980, analyzed October 7-12, 1980, spiked with chloramine-T.

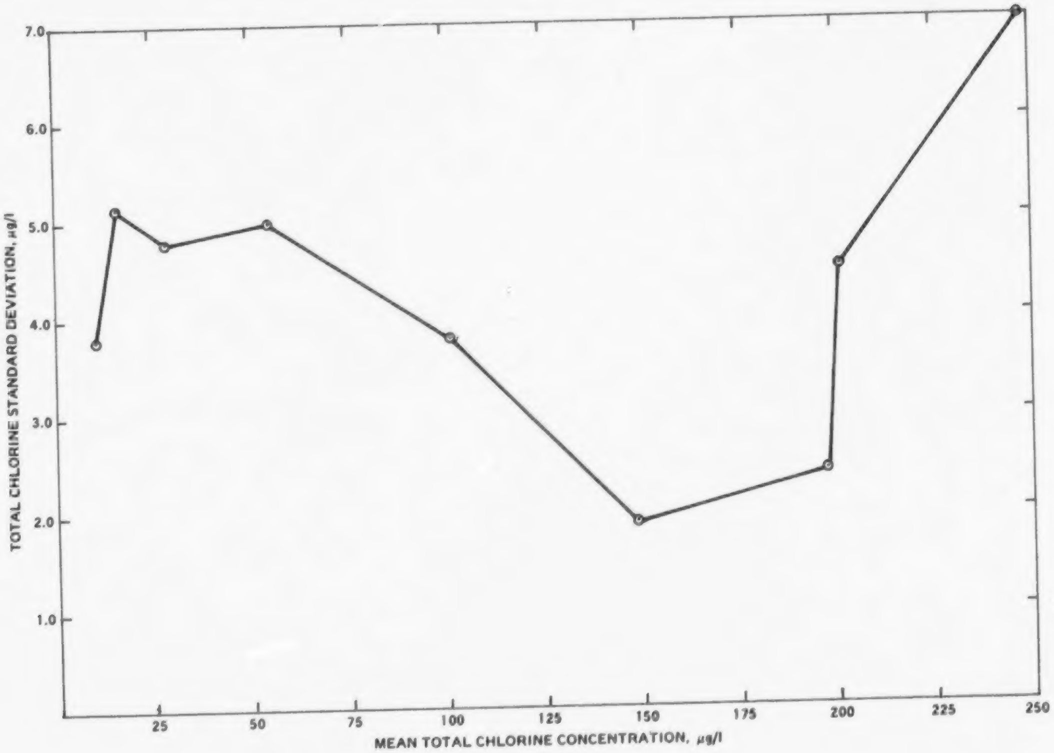

Figure 21. Total chlorine standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw Ross Landing surface river water sample collected October 3, 1980, analyzed October 7-12, 1980, spiked with chloramine-T.

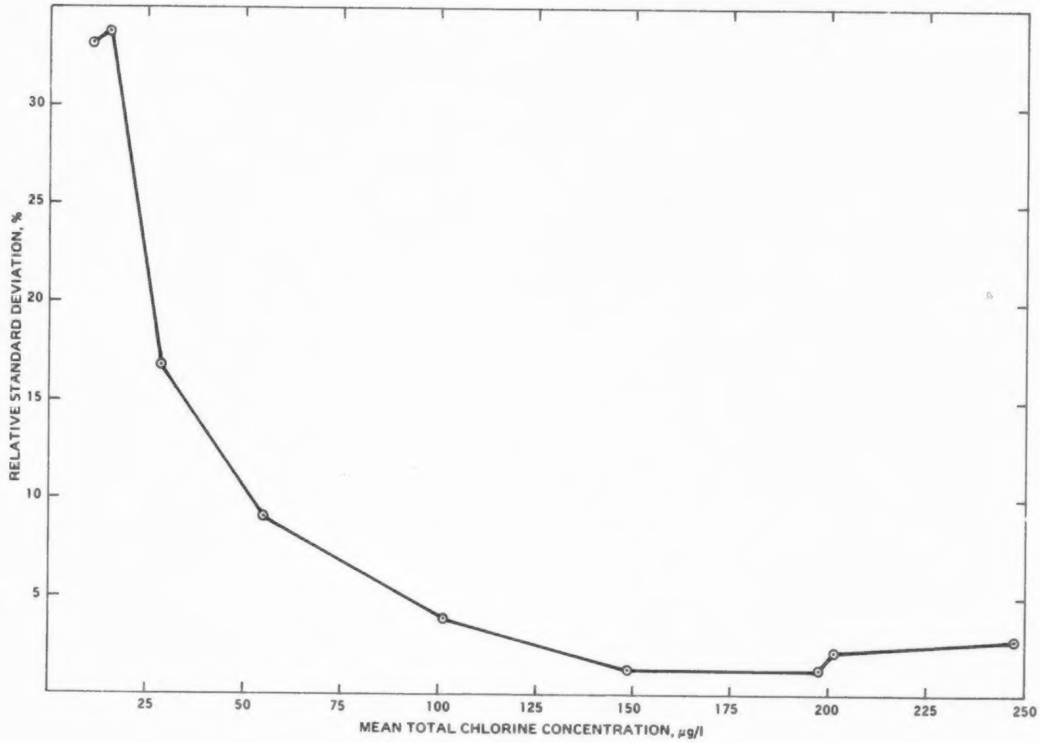

Figure 22. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw Ross Landing surface river water sample collected October 3, 1980, analyzed October 7-12, 1980, spiked with chloramine-T.

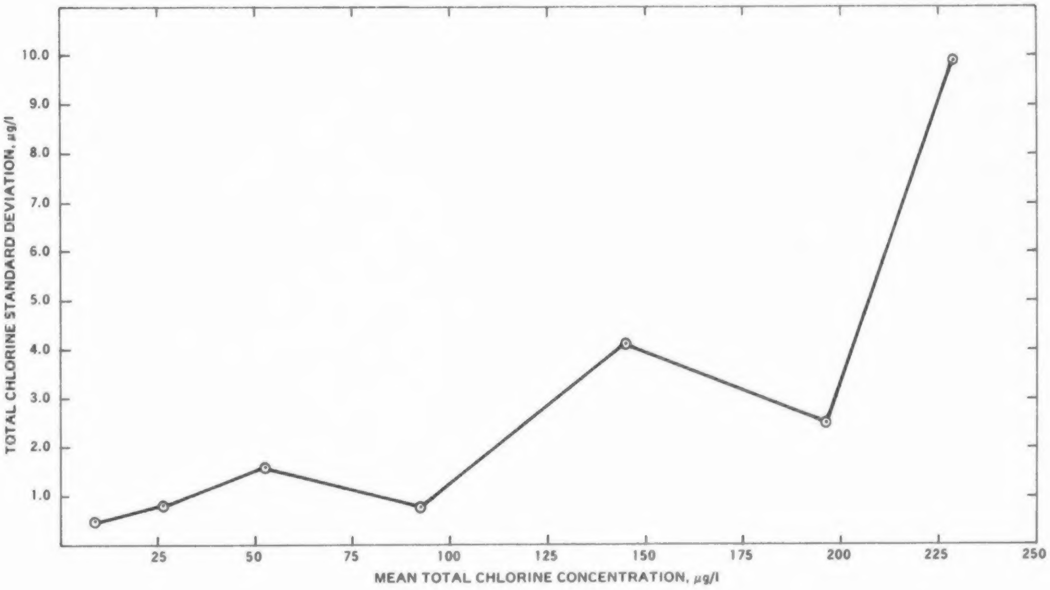

Figure 23. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw Ross Landing surface river water sample collected October 3, 1980, analyzed October 12, 1980, spiked with calcium hypochlorite.

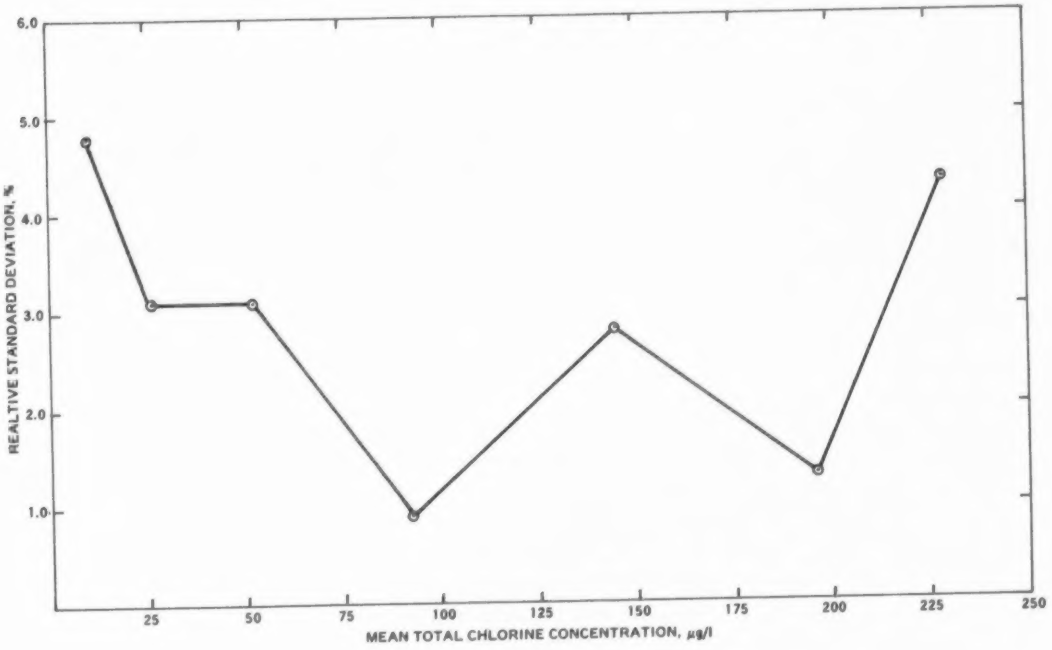

Figure 24. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw Ross Landing surface river water sample collected October 3, 1980, analyzed October 12, 1980, spiked with calcium hypochlorite.

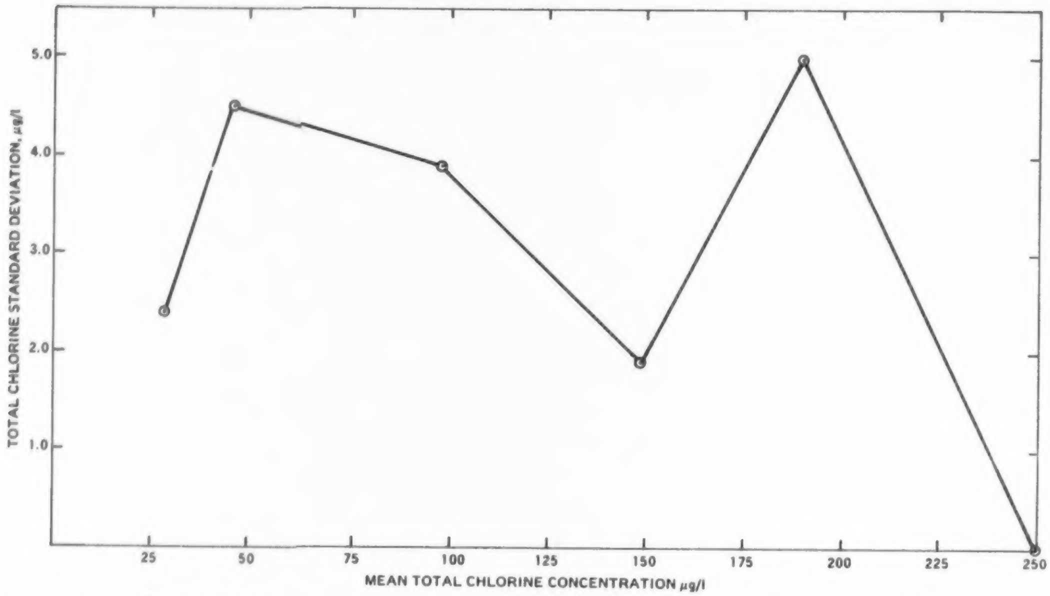

Figure 25. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration for experimental recovery by AT method of total chlorine from raw Ross Landing surface river water sample collected October 3, 1980, analyzed October 12, 1980, spiked with calcium hypochlorite.

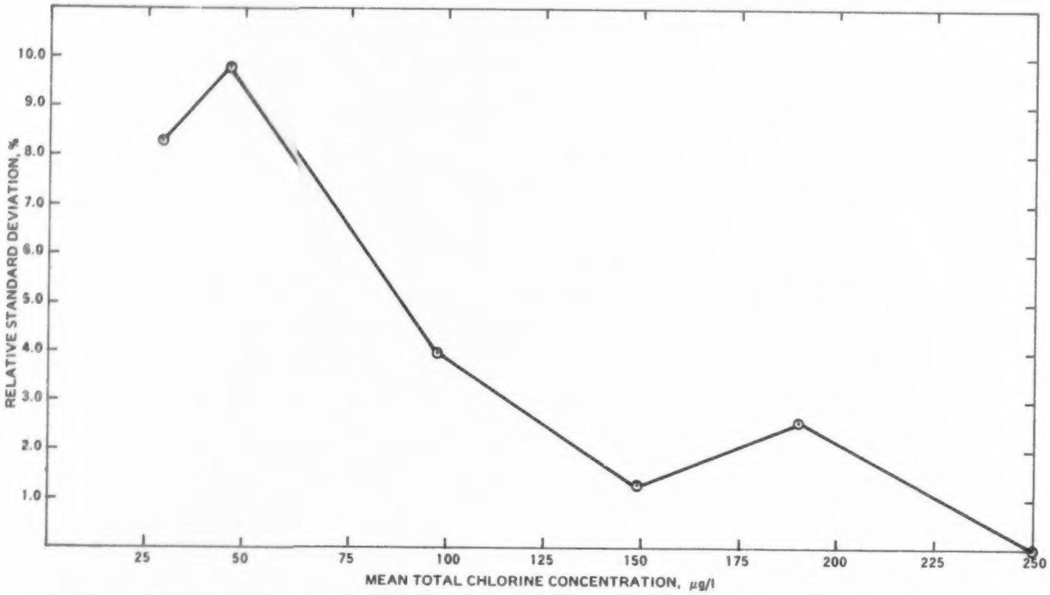

Figure 26. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw Ross Landing surface river water sample collected October 3, 1980, analyzed October 12, 1980, spiked with calcium hypochlorite.

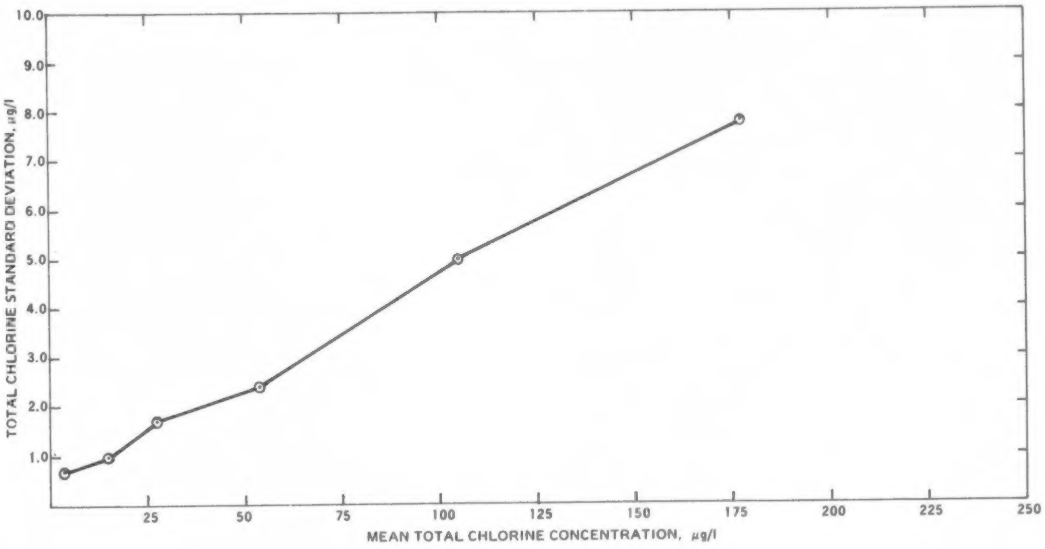

Figure 27. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Kingston Steam Plant condenser cooling river water samples analyzed October 15-16, 1980.

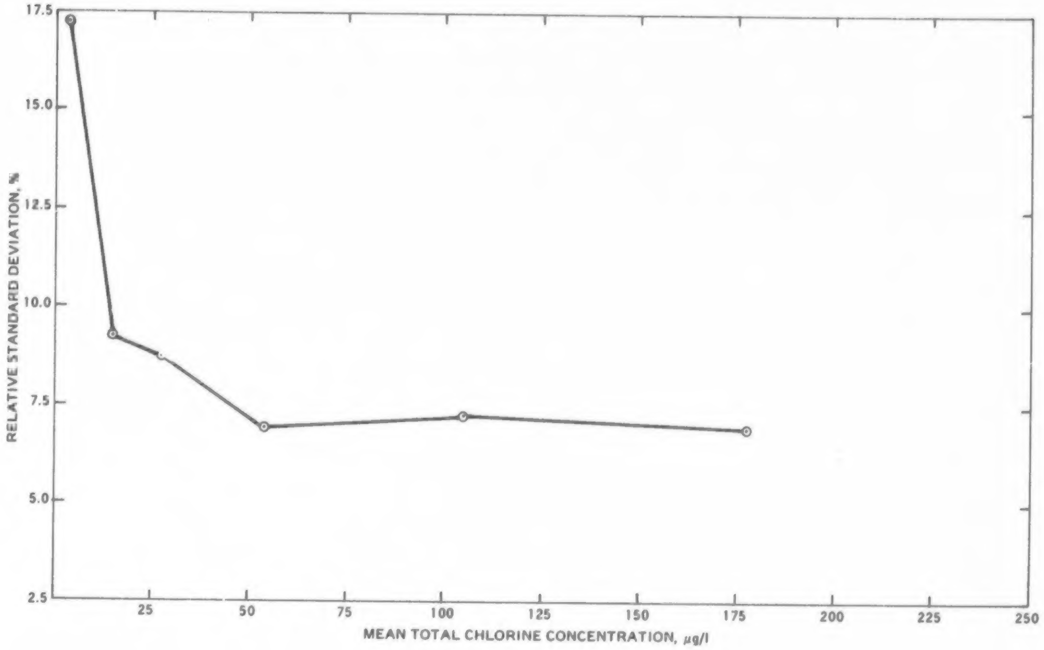

Figure 28. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Kingston Steam Plant condenser cooling river water samples analyzed October 15-16, 1980.

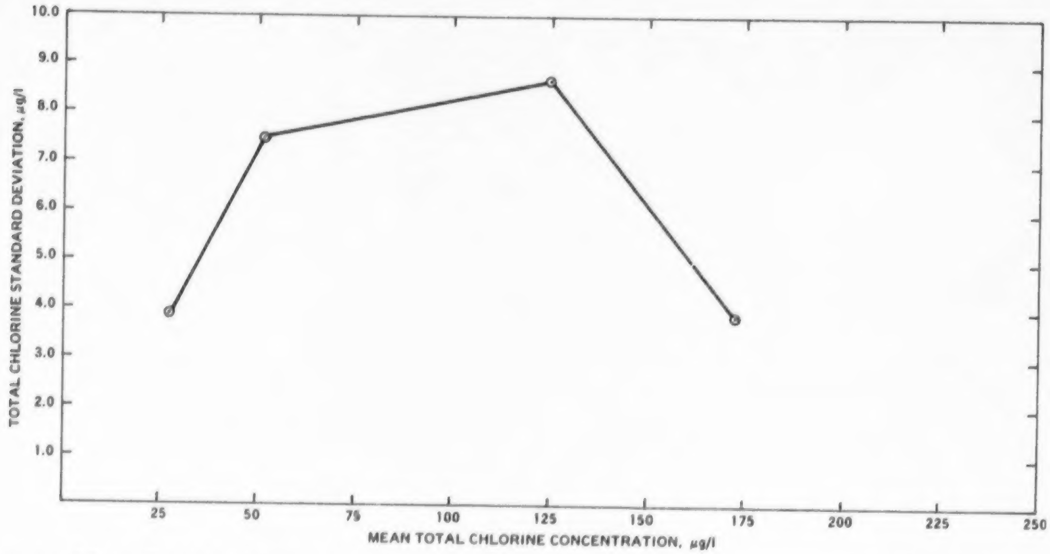

Figure 29. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Kingston Steam Plant condenser cooling river water samples analyzed October 15-16, 1980.

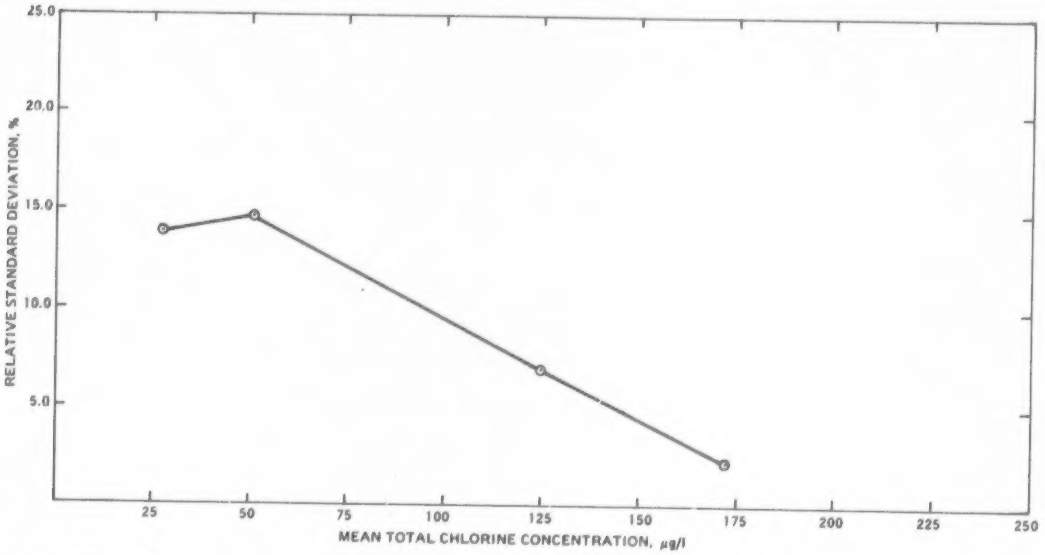

Figure 30. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Kingston Steam Plant condenser cooling river water samples analyzed October 15-16, 1980.

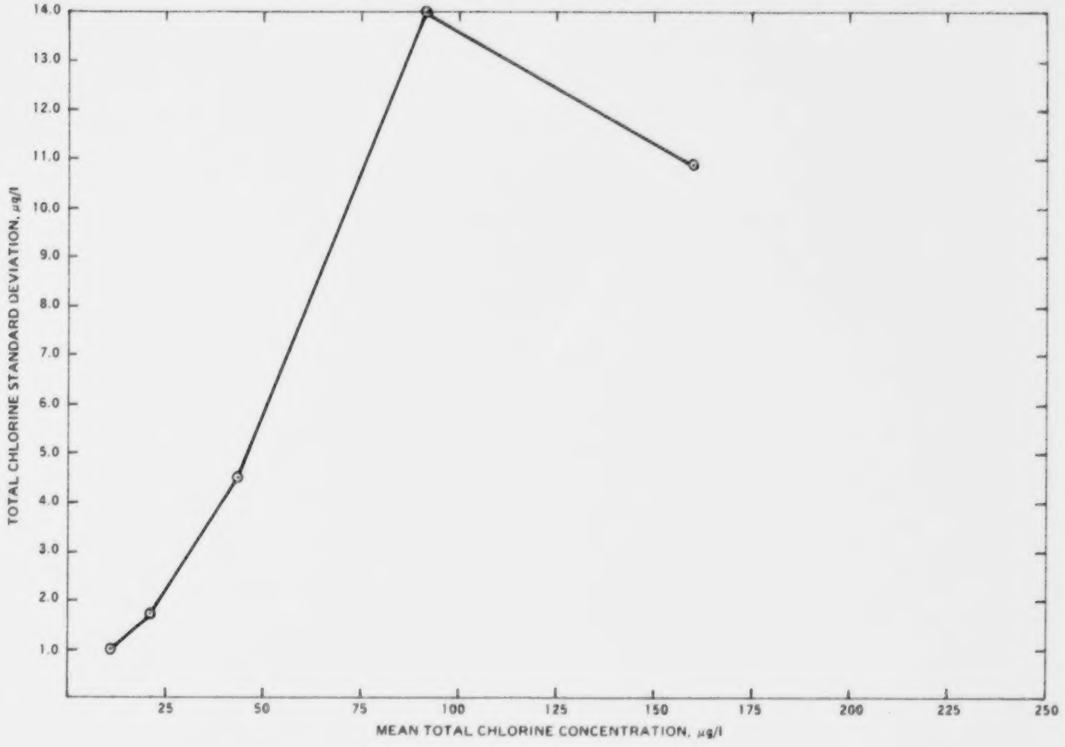

Figure 31. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Kingston Steam Plant condenser cooling river water samples analyzed October 15-16, 1980, spiked with calcium hypochlorite.

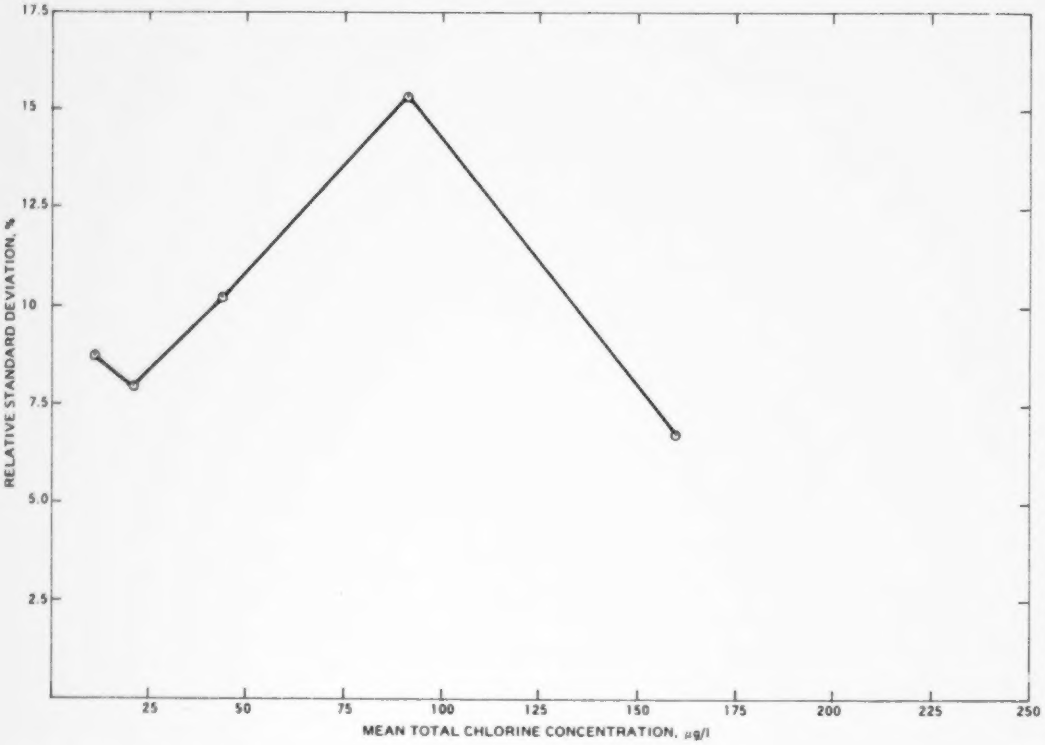

Figure 32. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Kingston Steam Plant condenser cooling river water samples analyzed October 15-16, 1980, spiked with calcium hypochlorite.

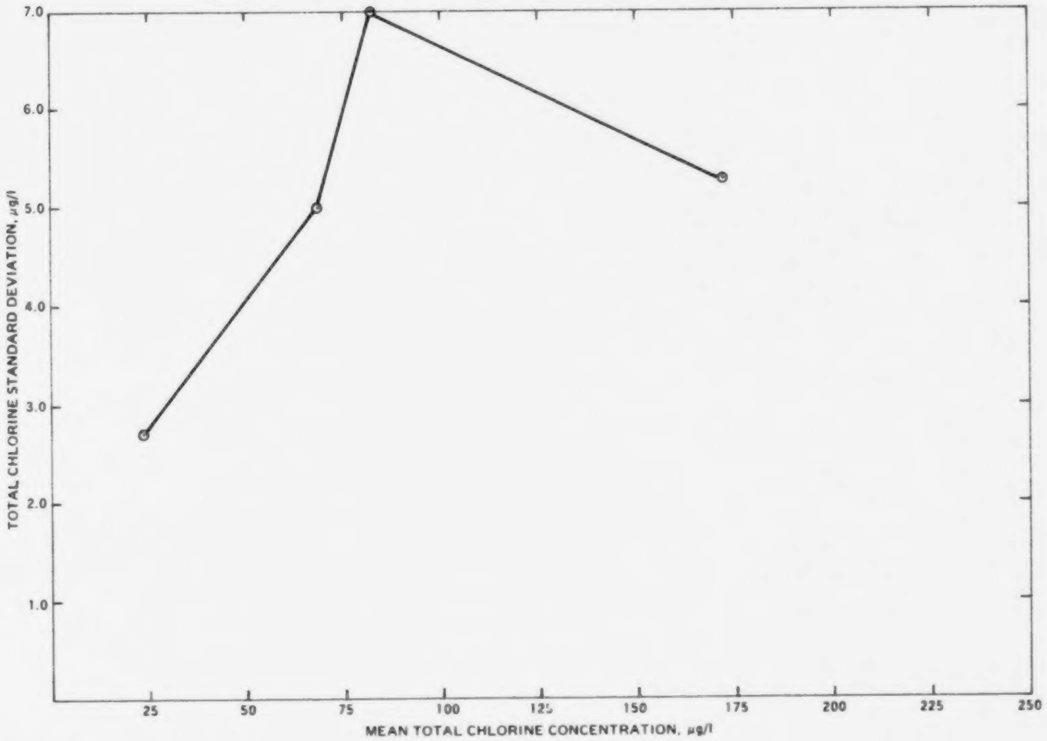

Figure 33. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Kingston Steam Plant condenser cooling river water samples analyzed October 15-16, 1980, spiked with calcium hypochlorite.

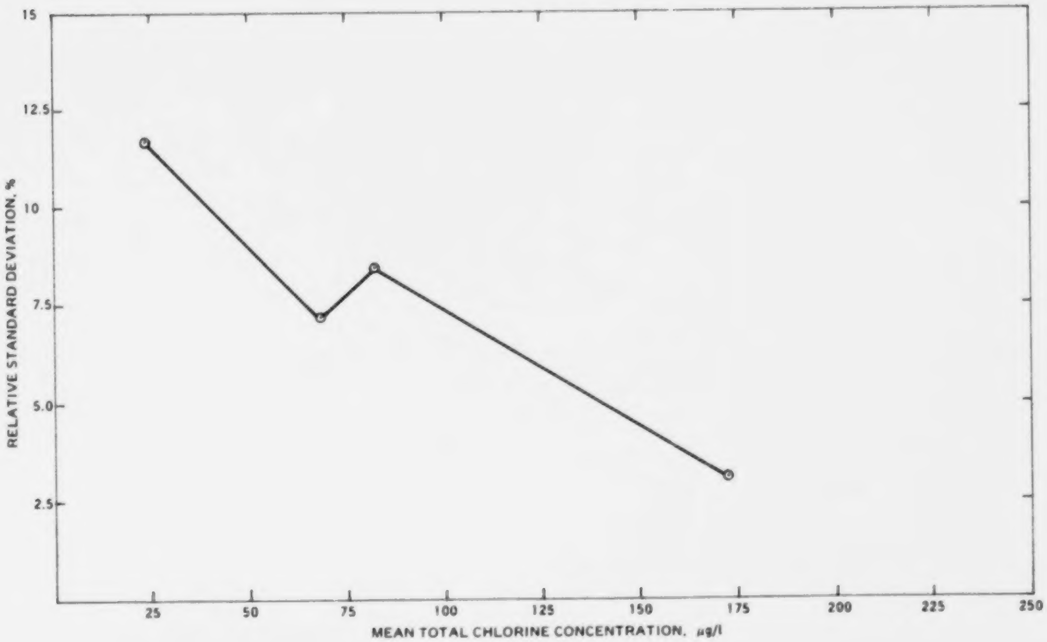

Figure 34. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Kingston Steam Plant condenser cooling river water samples analyzed October 15-16, 1980, spiked with calcium hypochlorite.

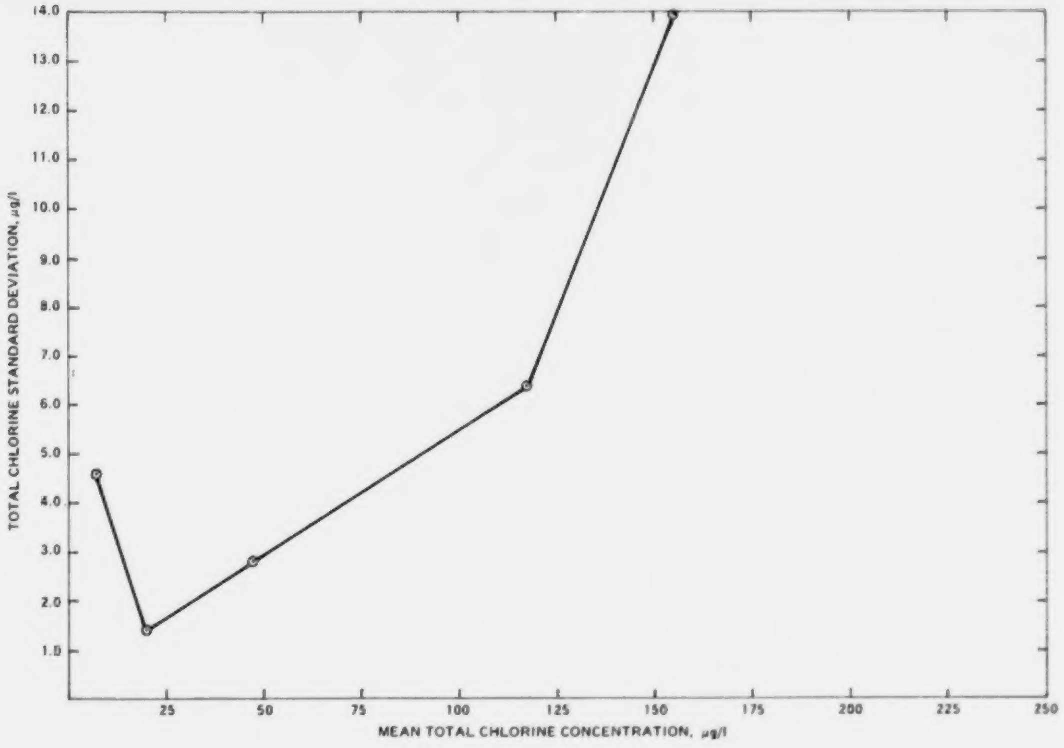

Figure 35. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Shawnee Steam Plant condenser cooling river water samples analyzed October 21-22, 1980.

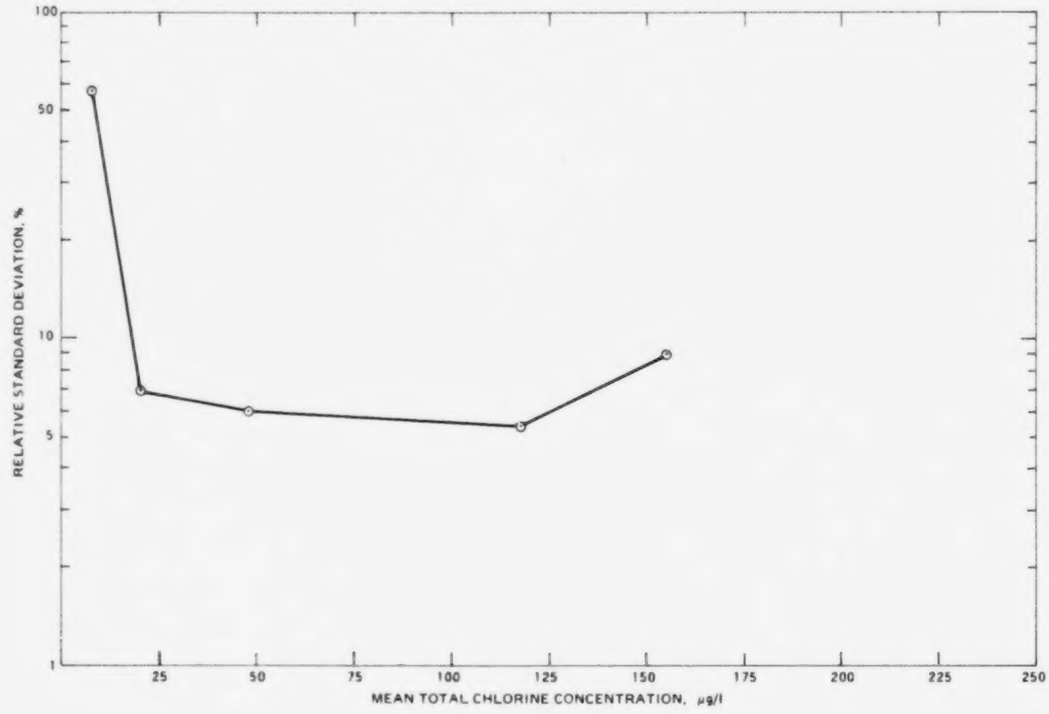

Figure 36. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Shawnee Steam Plant condenser cooling river water samples analyzed October 21-22, 1980.

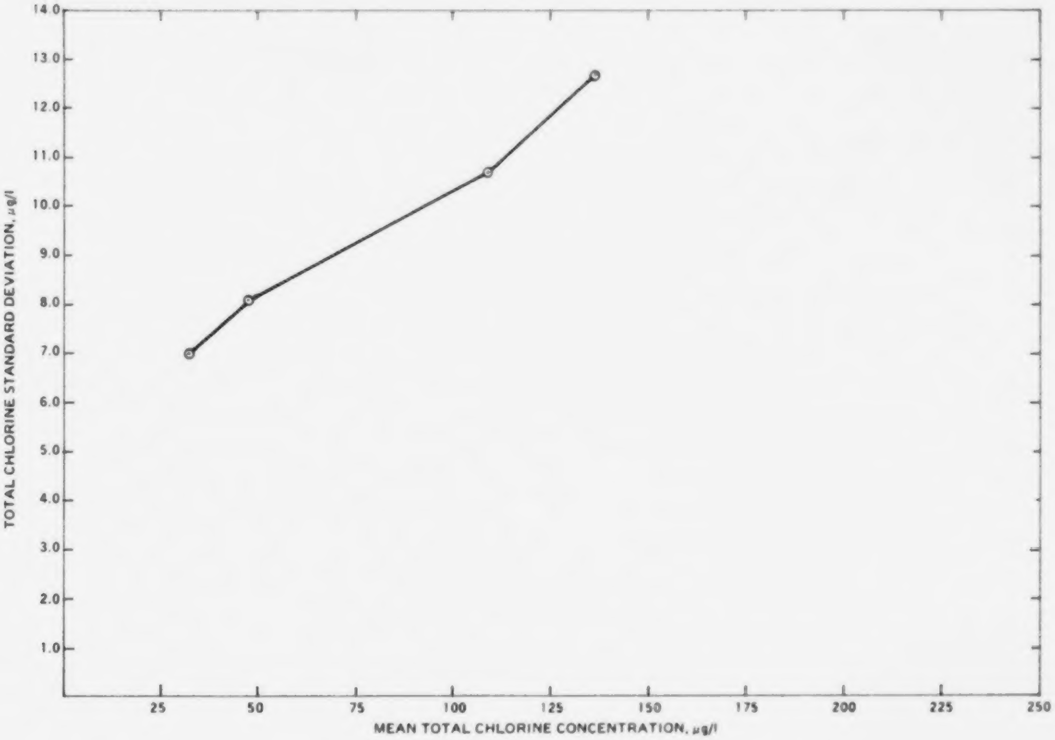

Figure 37. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Shawnee Steam Plant condenser cooling river water samples analyzed October 21-22, 1980.

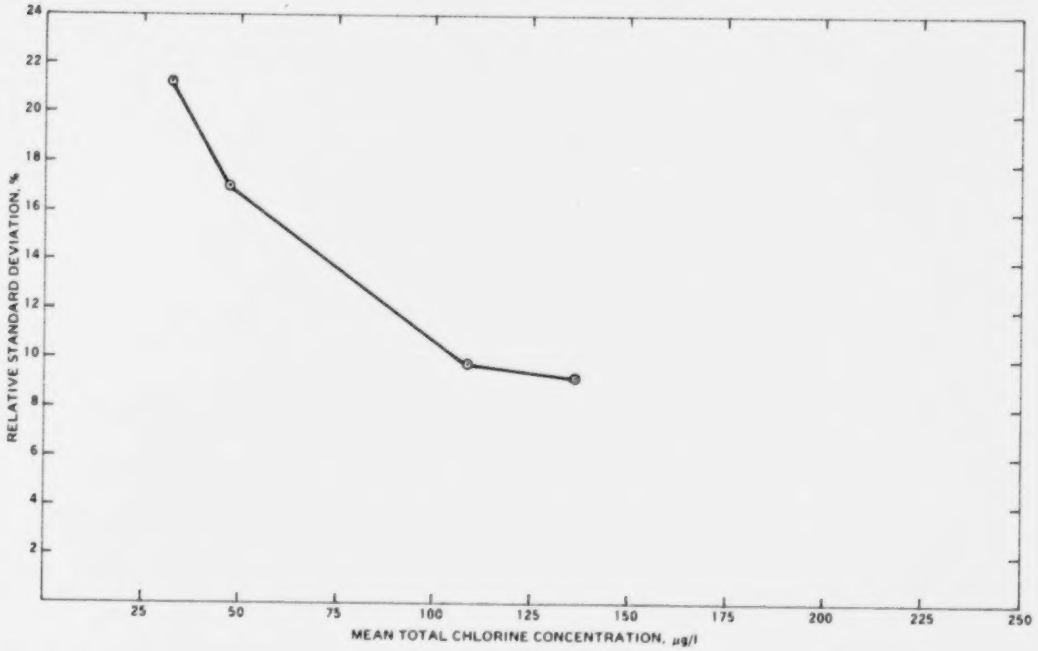

Figure 38. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Shawnee Steam Plant condenser cooling river water samples analyzed October 21-22, 1980.

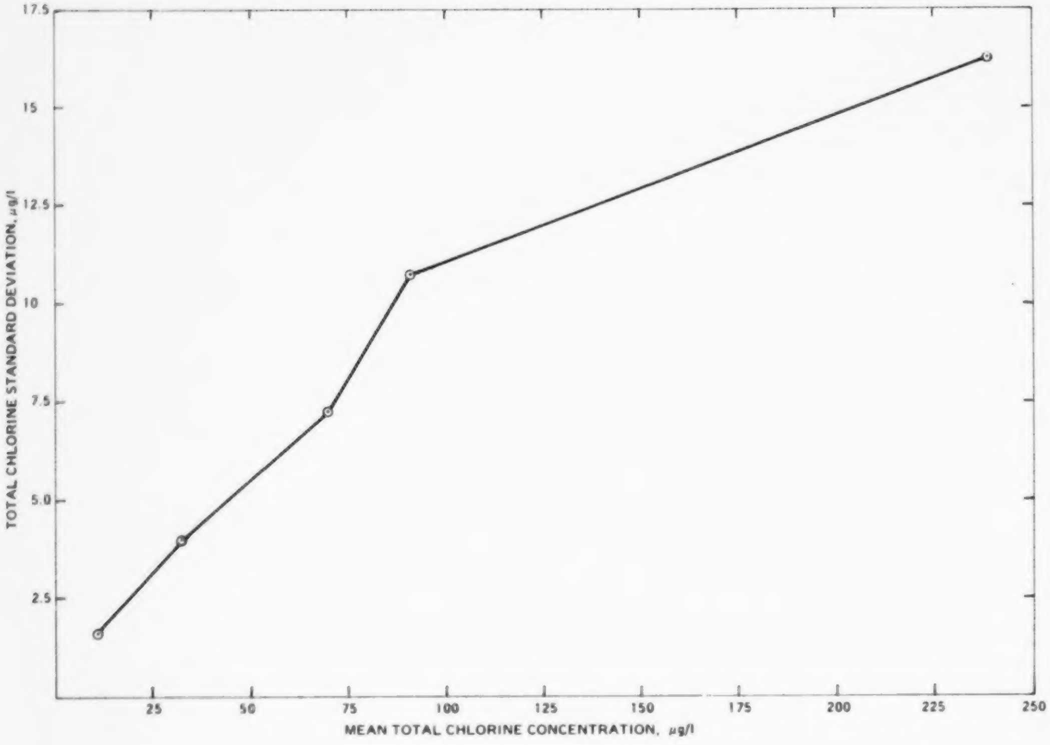

Figure 39. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Shawnee Steam Plant condenser cooling river water samples analyzed October 21-22, 1980, spiked with calcium hypochlorite.

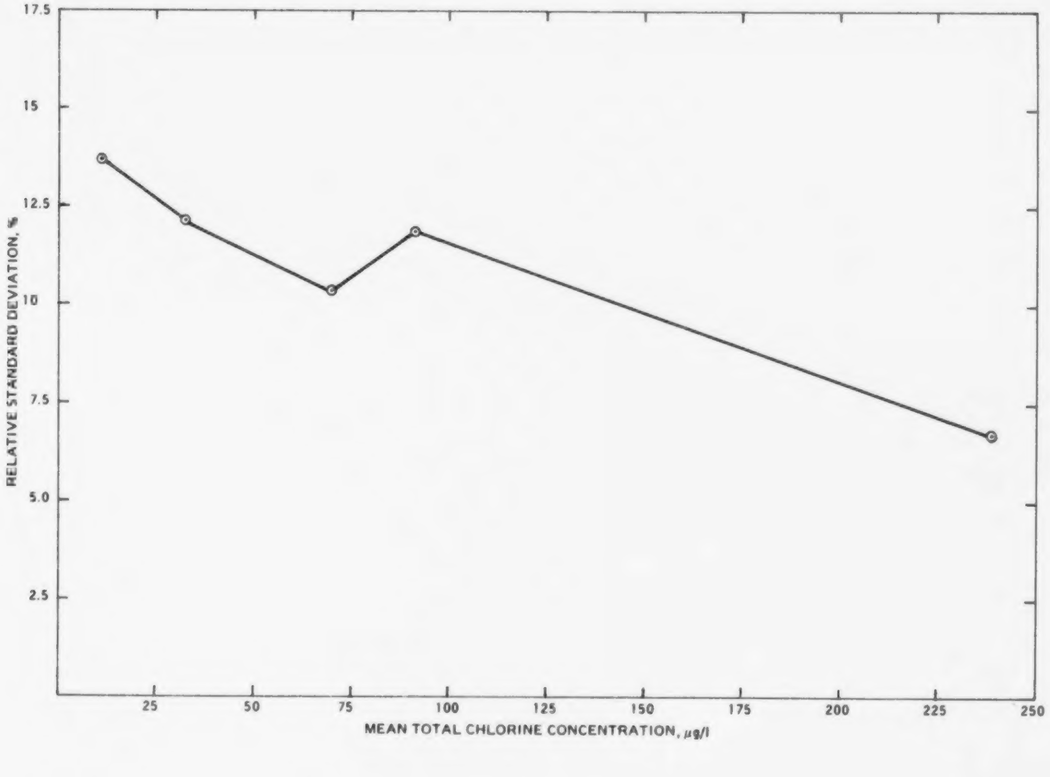

Figure 40. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Shawnee Steam Plant condenser cooling river water samples analyzed October 21-22, 1980, spiked with calcium hypochlorite.

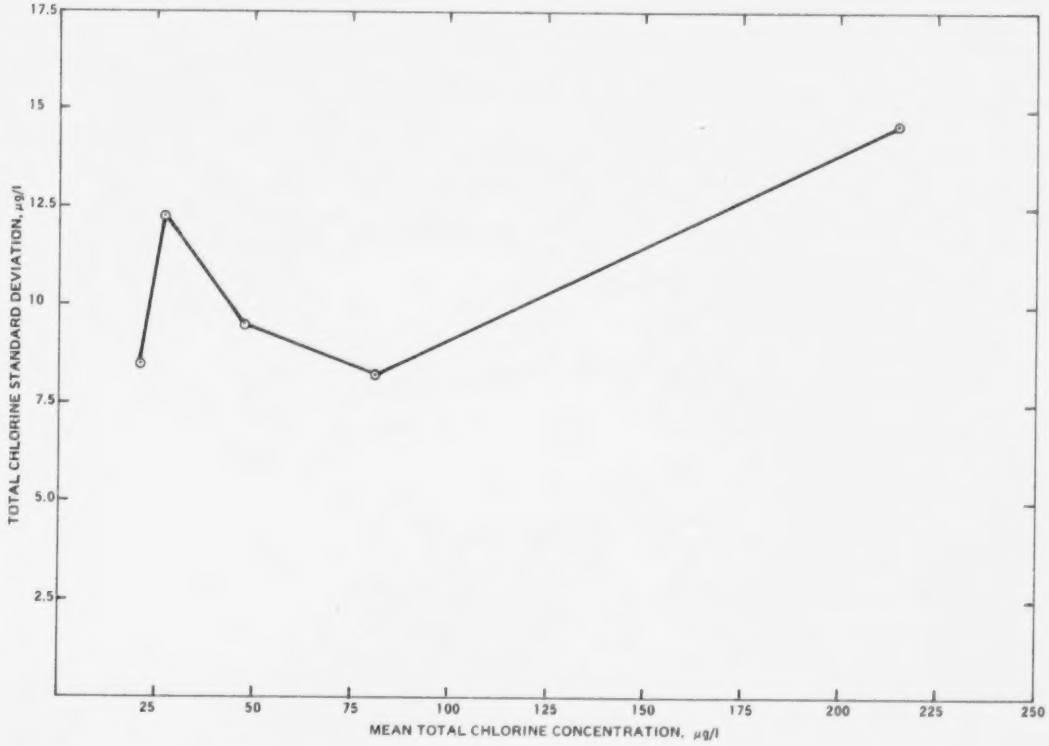

Figure 41. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Shawnee Steam Plant condenser cooling river water samples analyzed October 21-22, 1980, spiked with calcium hypochlorite.

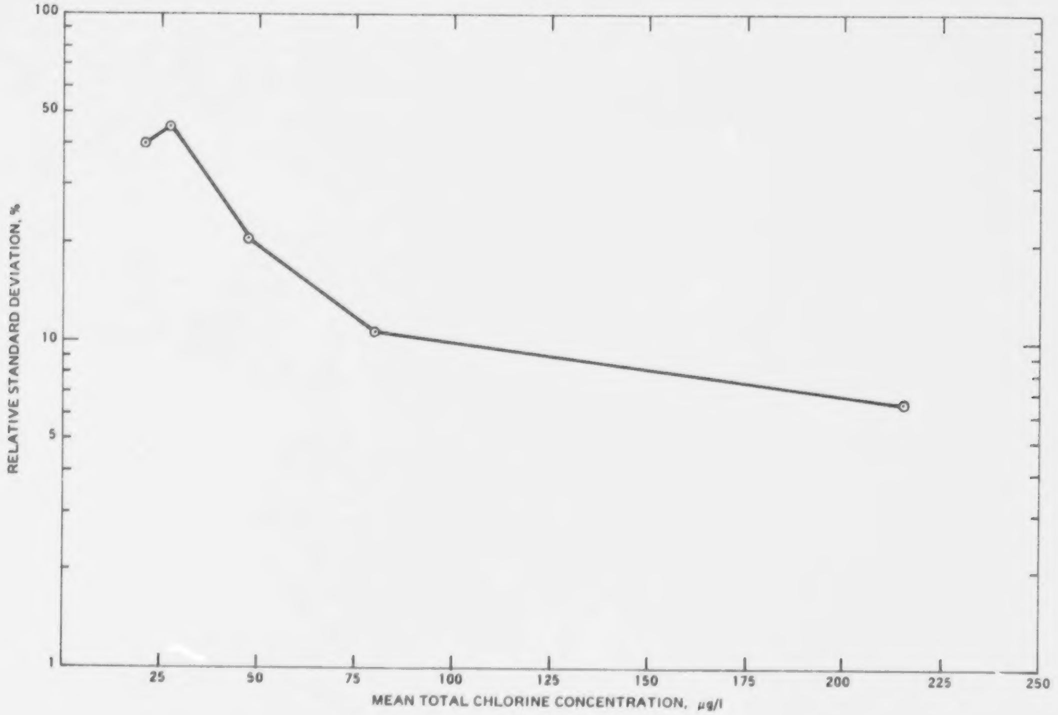

Figure 42. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Shawnee Steam Plant condenser cooling river water samples analyzed October 21-22, 1980, spiked with calcium hypochlorite.

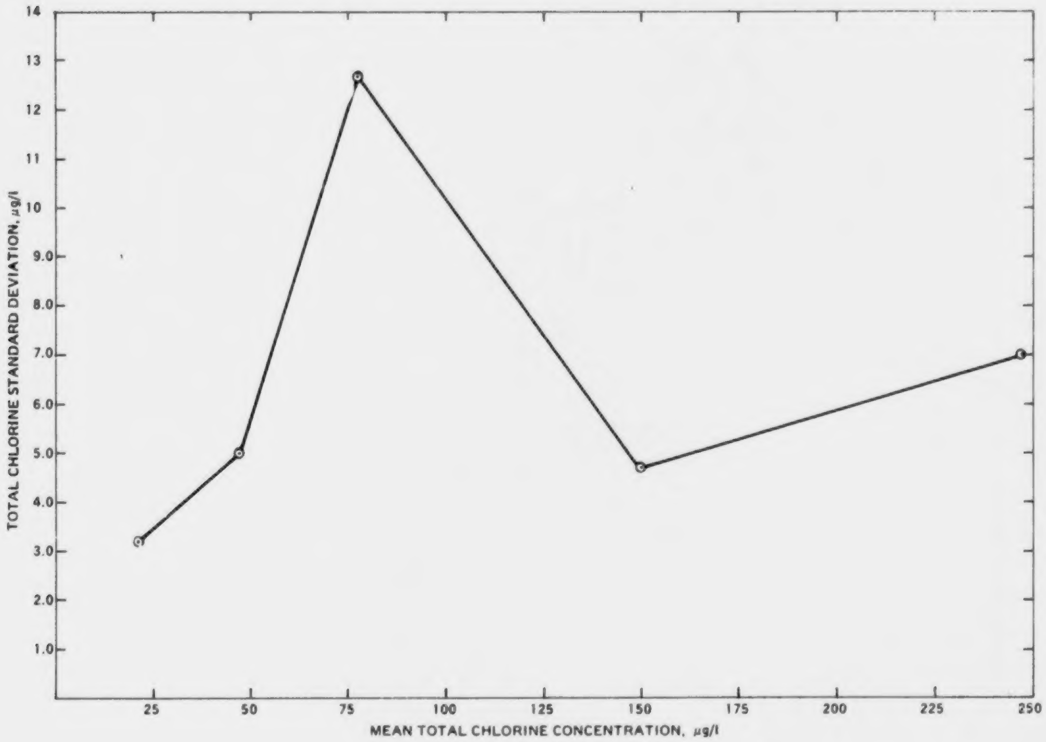

Figure 43. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Allen Steam Plant condenser cooling river water samples analyzed October 28-29, 1980.

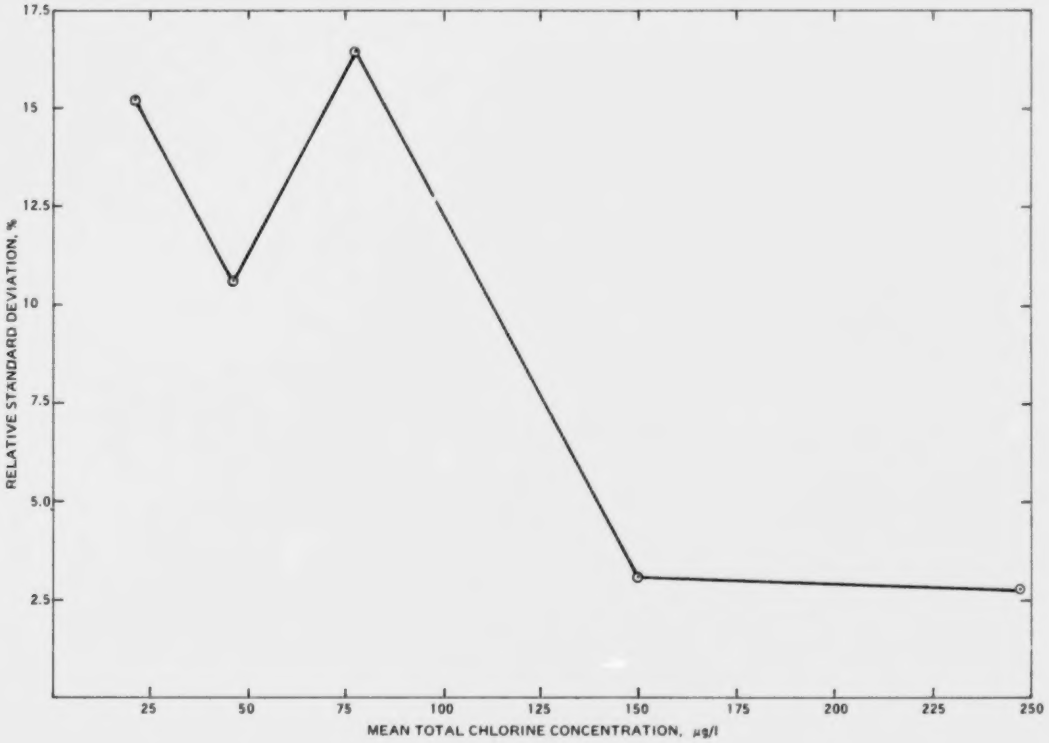

Figure 44. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Allen Steam Plant condenser cooling river water samples analyzed October 28-29, 1980.

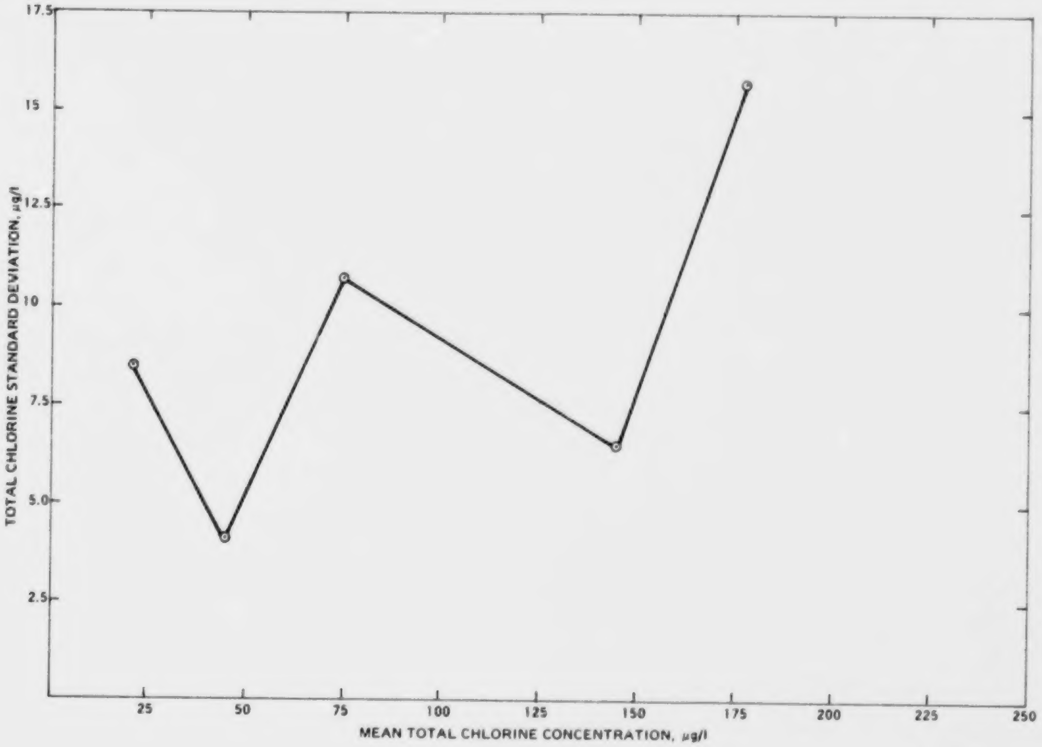

Figure 45. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Allen Steam Plant condenser cooling river water samples analyzed October 28-29, 1980.

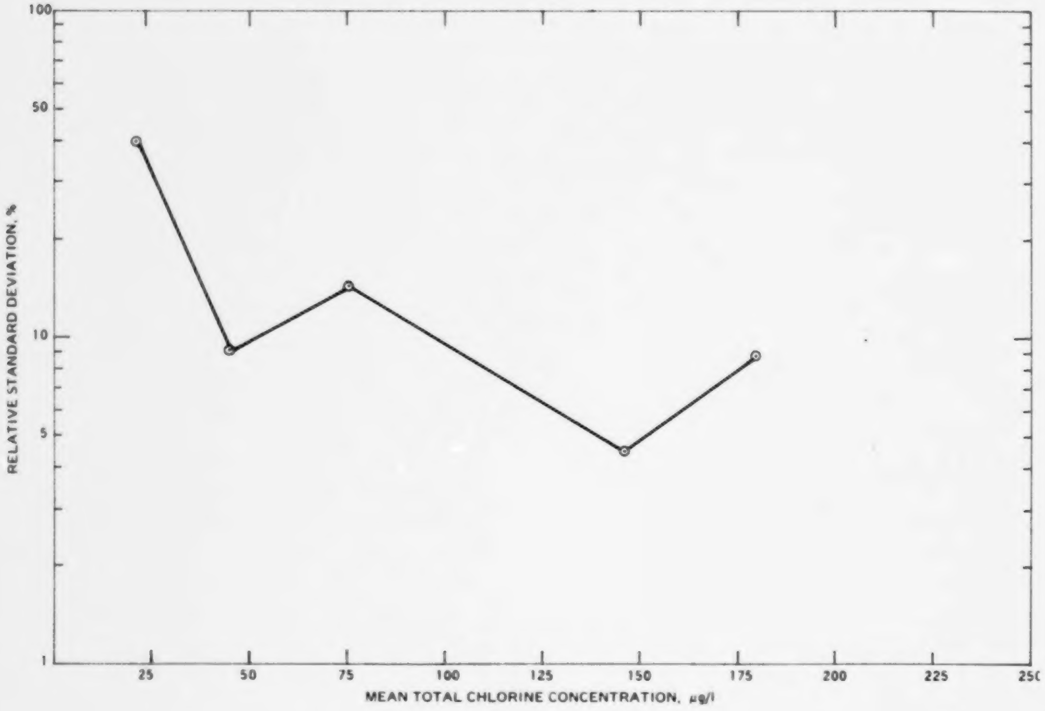

Figure 46. Percentage relative standard deviation against mean concentration for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Allen Steam Plant condenser cooling river water samples analyzed October 28-29, 1980.

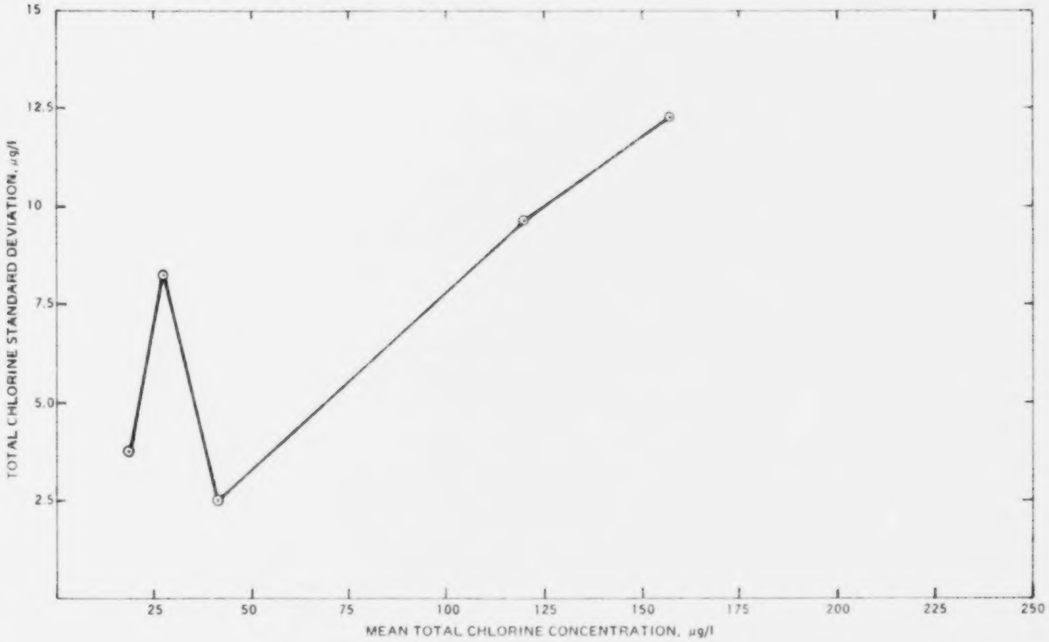

Figure 47. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Allen Steam Plant condenser cooling river water samples analyzed October 28-29, 1980, spiked with calcium hypochlorite.

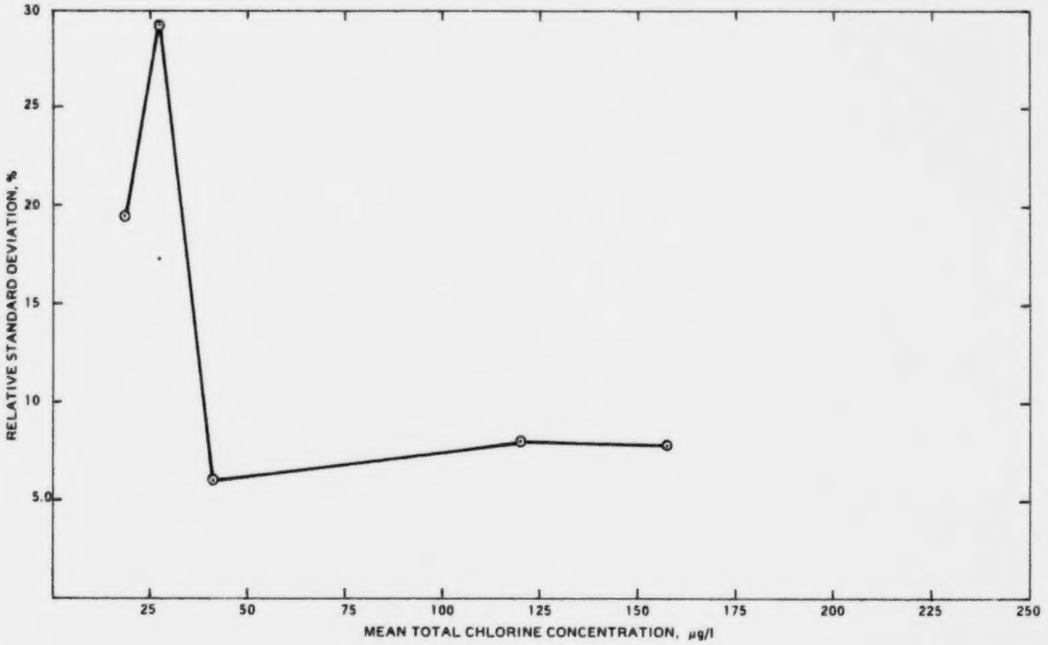

Figure 48. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Allen Steam Plant condenser cooling river water samples analyzed October 28-29, 1980, spiked with calcium hypochlorite.

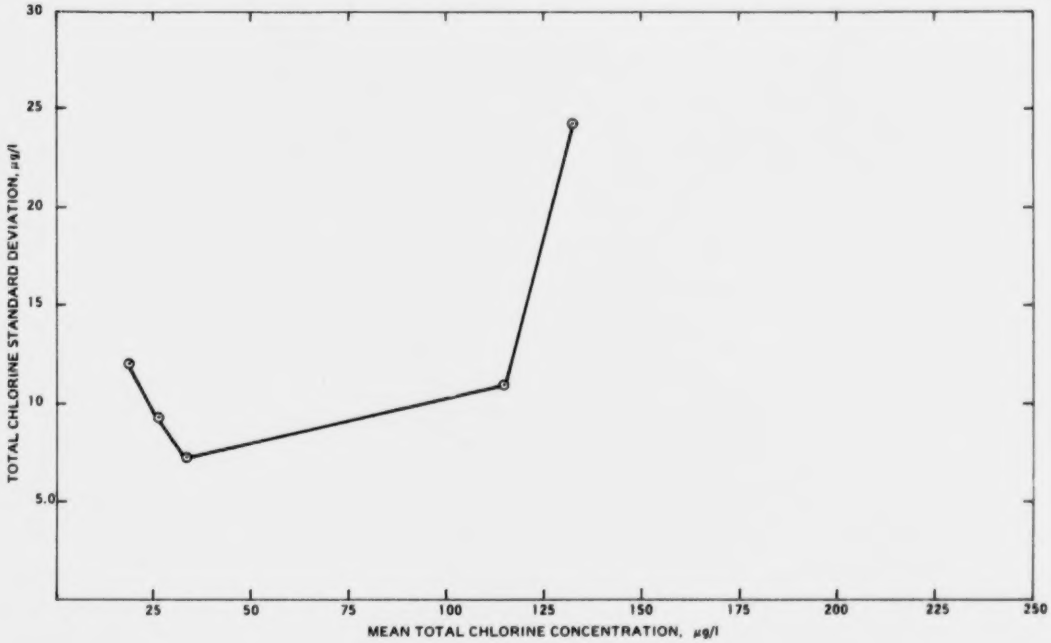

Figure 49. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Allen Steam Plant condenser cooling river water samples analyzed October 28-29, 1980, spiked with calcium hypochlorite.

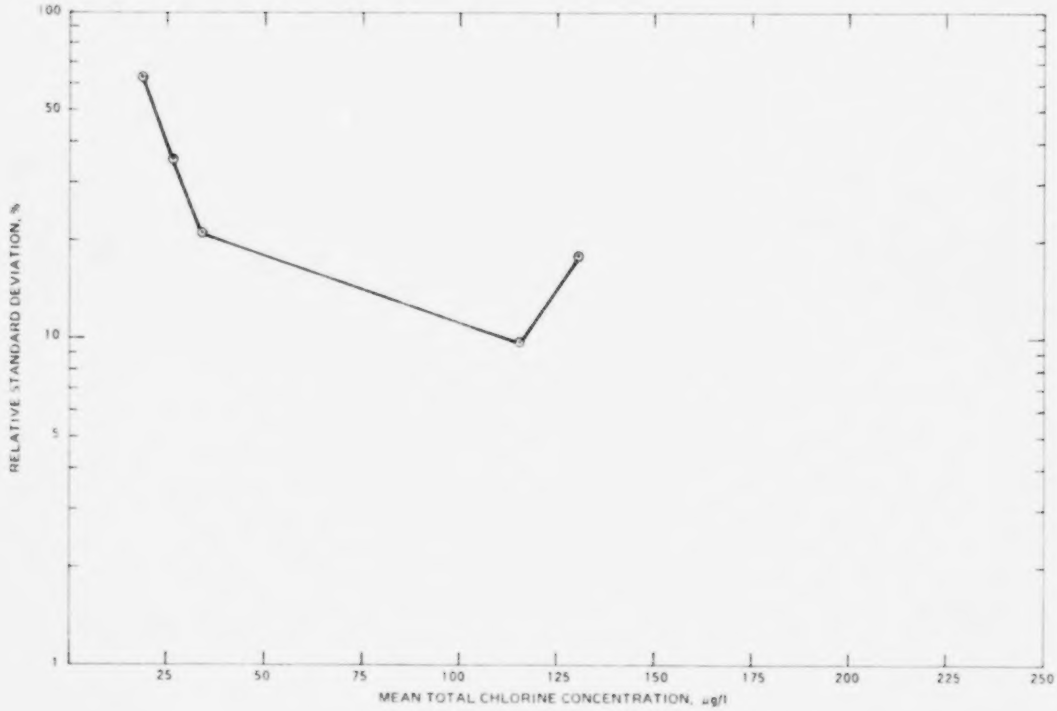

Figure 50. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated Allen Steam Plant condenser cooling river water samples analyzed October 28-29, 1980, spiked with calcium hypochlorite.

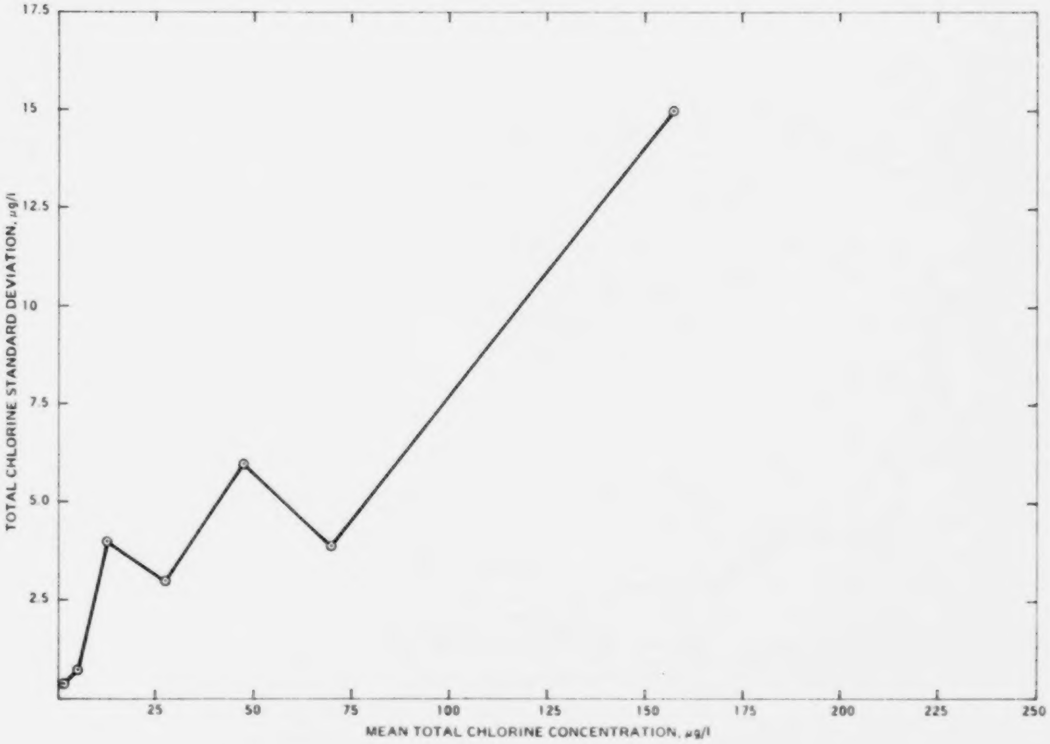

Figure 51. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated John Sevier Steam Plant condenser cooling river water samples analyzed November 4-5, 1980.

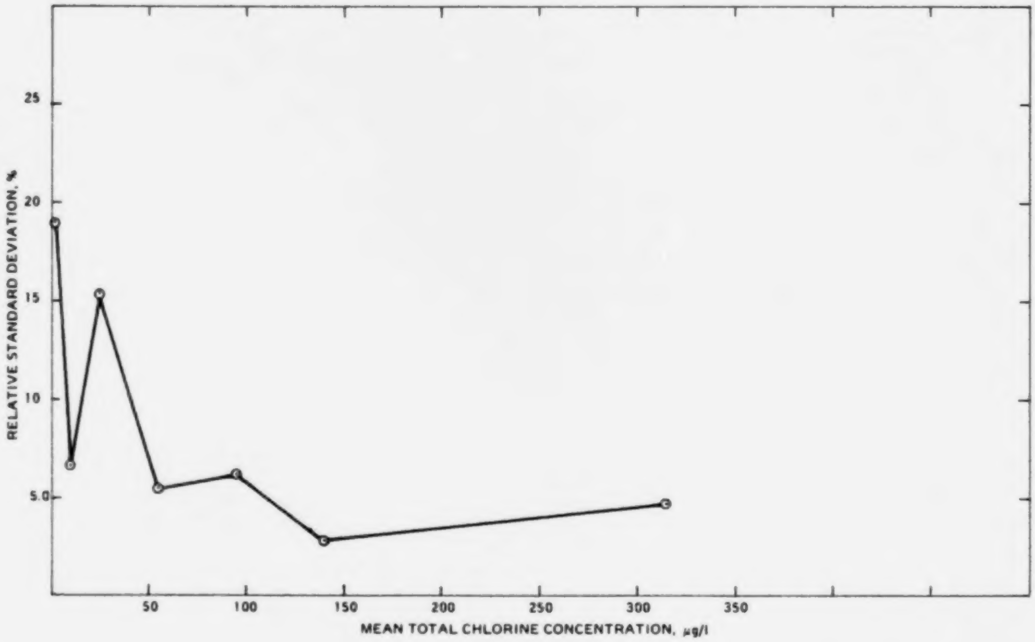

Figure 52. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated John Sevier Steam Plant condenser cooling river water samples analyzed November 4-5, 1980.

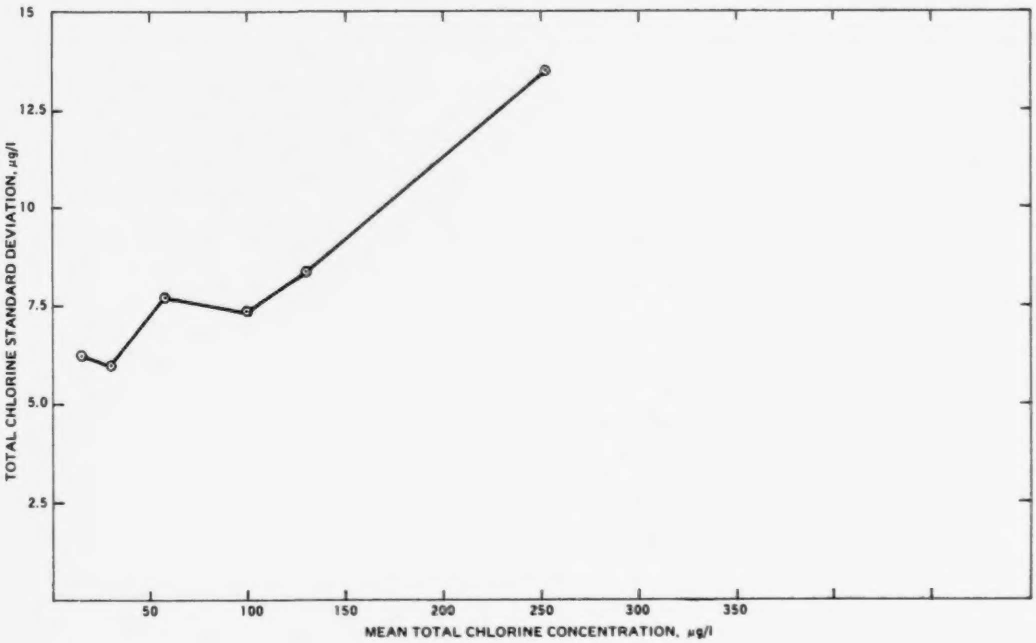

Figure 53. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated John Sevier Steam Plant condenser cooling river water samples analyzed November 4-5, 1980.

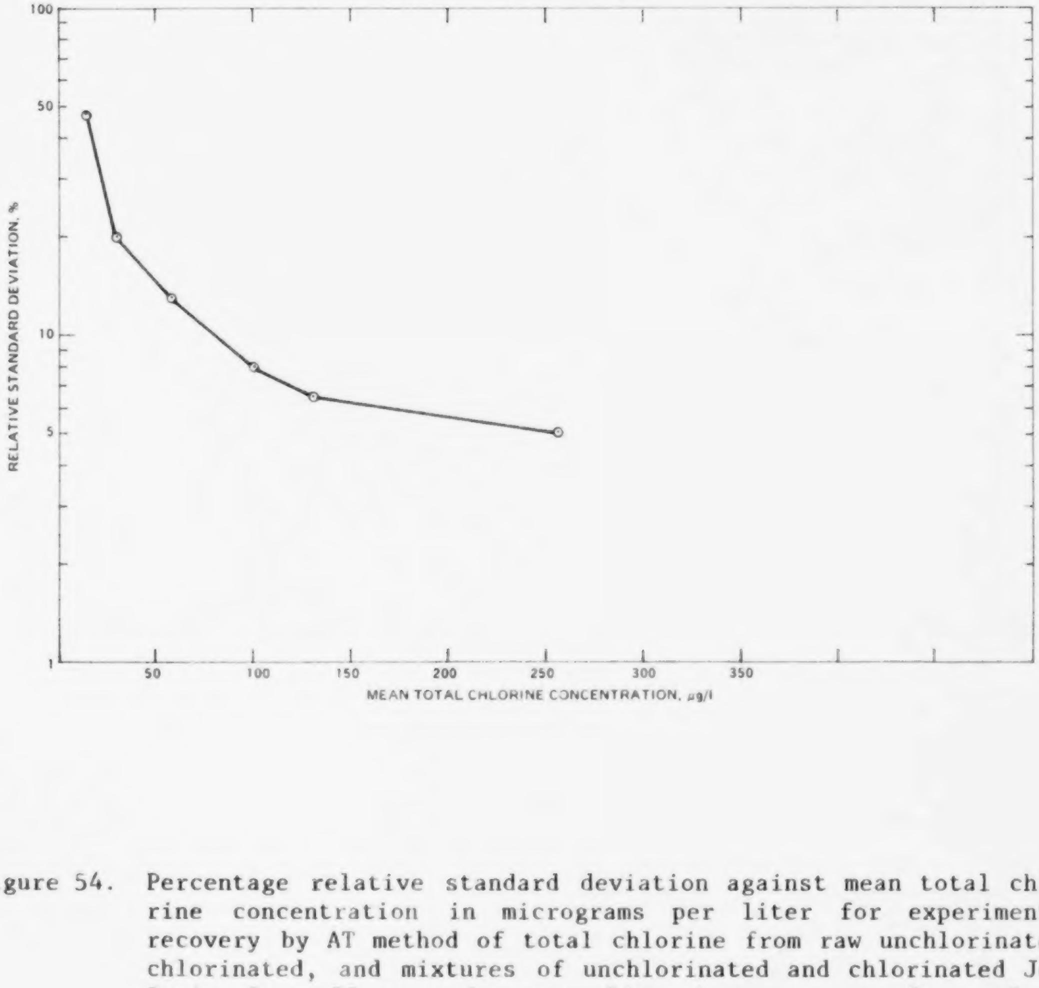

Figure 54. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated John Sevier Steam Plant condenser cooling river water samples analyzed November 4-5, 1980.

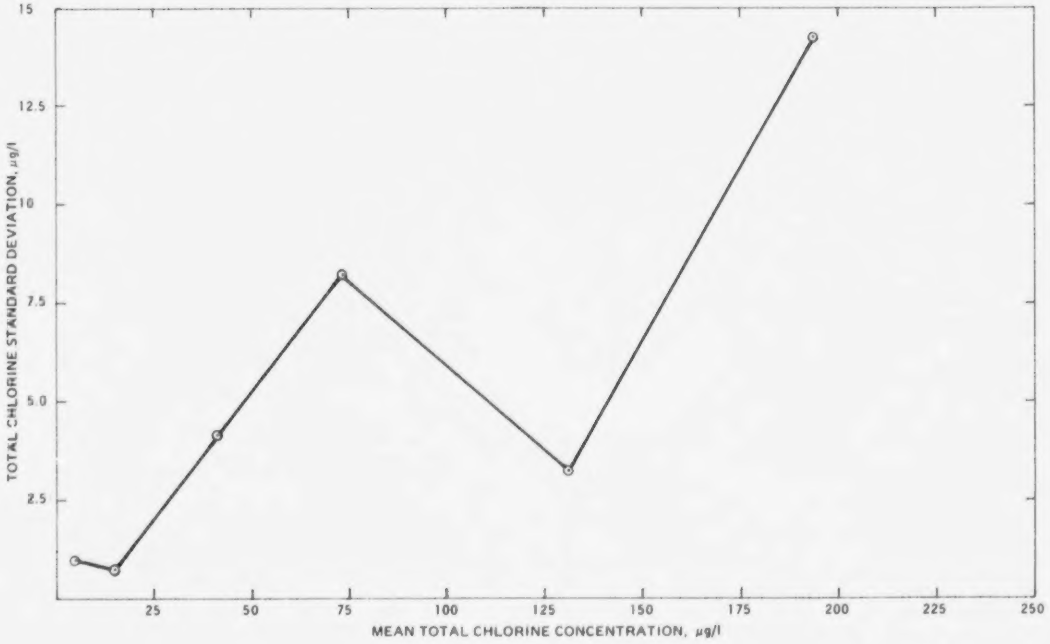

Figure 55. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated John Sevier Steam Plant condenser cooling river water samples analyzed November 4-5, 1980, spiked with calcium hypochlorite.

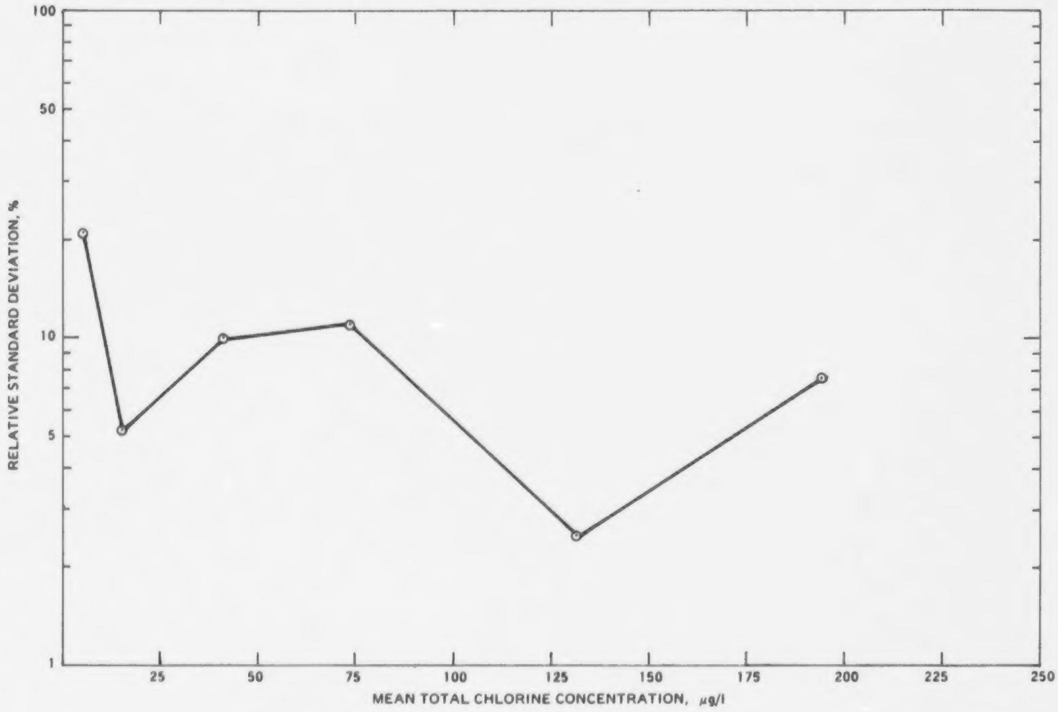

Figure 56. Percentage relative standard deviation against mean total chlorine concentration in micrograms per liter for experimental recovery by MC method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated John Sevier Steam Plant condenser cooling river water samples analyzed November 4-5, 1980, spiked with calcium hypochlorite.

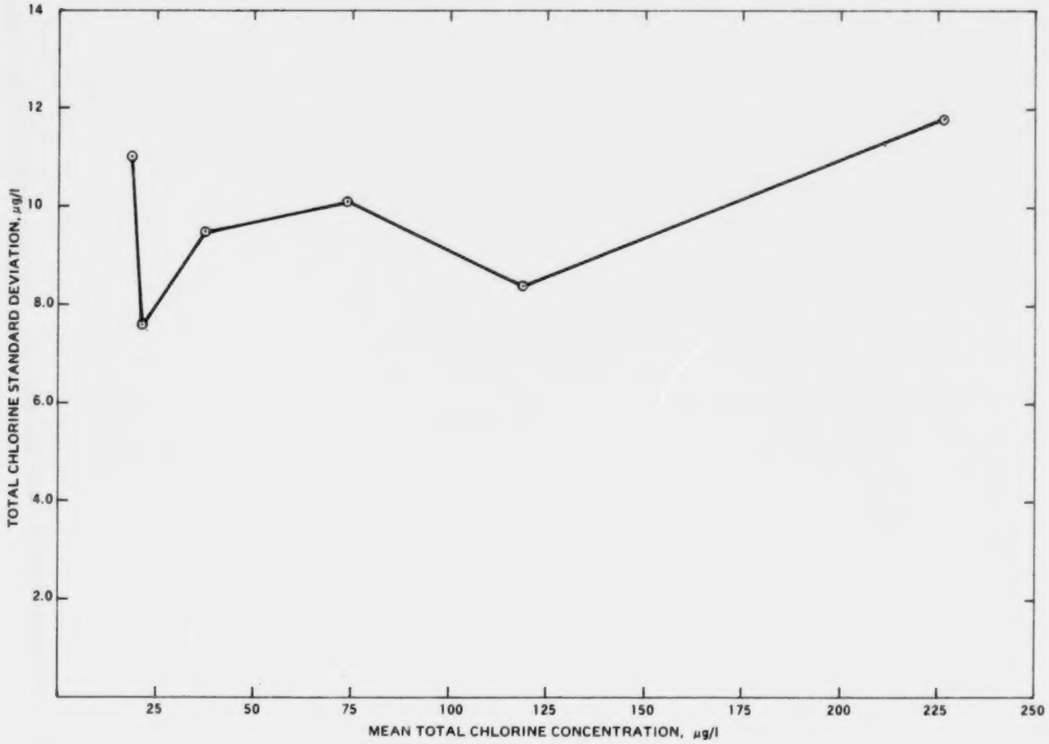

Figure 57. Total chlorine standard deviation in micrograms per liter against mean total chlorine concentration in micrograms per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated John Sevier Steam Plant condenser cooling river water samples analyzed November 4-5, 1980, spiked with calcium hypochlorite.

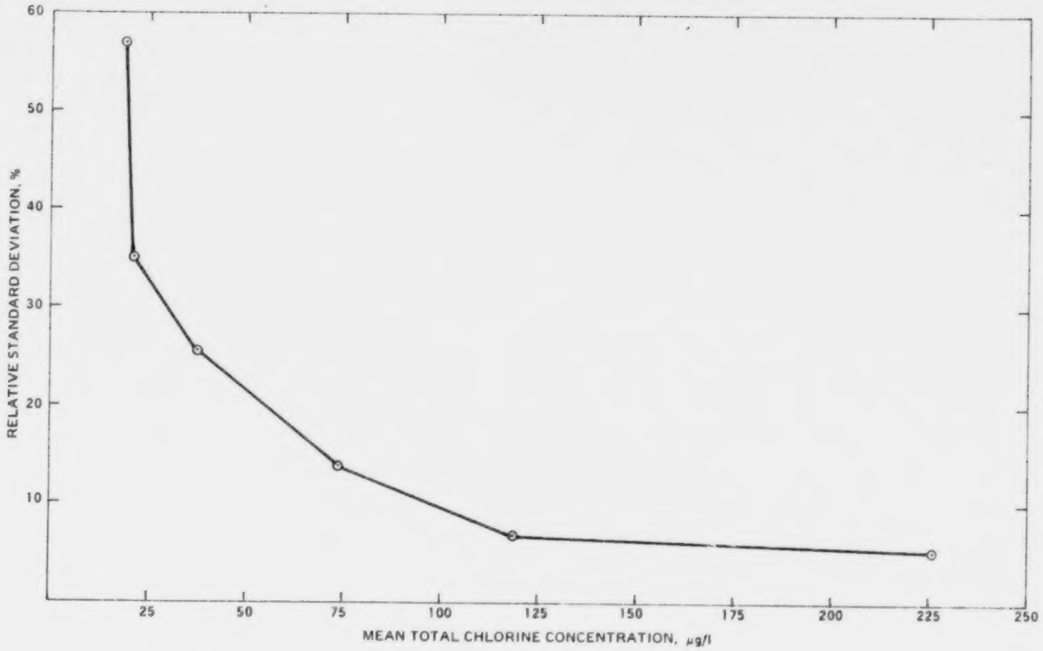

Figure 58. Percentage relative standard deviation against mean total chlorine concentration in micrgrams per liter for experimental recovery by AT method of total chlorine from raw unchlorinated, chlorinated, and mixtures of unchlorinated and chlorinated John Sevier Steam Plant condenser cooling river water samples analyzed November 4-5, 1980, spiked with calcium hypochlorite.

Tables

TABLE 1. SPIKING EXPERIMENTS WITH CHLORAMINE-T OR CALCIUM HYPOCHLORITE FOR PRECISION AND ACCURACY TESTS OF THE MC METHOD

Chlorine[a] spiking solution (mg/l)	Volume of solution spiked (ml)	Volume of spiking solution, (µl)	Final concentration of chlorine (µg/l)	Aliquot for dilution (ml)	Volume of deionized water added (ml)	Expected concentration of chlorine (µg/l)	Dilution factor
12.5	50	0	0	None	None	Same	None
12.5	50	20	5	None	None	Same	None
12.5	50	40	10	None	None	Same	None
12.5	50	100	25	None	None	Same	None
12.5	50	200	50	None	None	Same	None
12.5	50	400	99	None	None	Same	None
12.5	50	600	148	20	30	59	2.5
12.5	50	800	197	20	30	79	2.5
12.5	50	1000	245	10	40	49	5

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[a] Chloramine-T or calcium hypochlorite as chlorine.

TABLE 2. SPIKING EXPERIMENTS WITH CHLORAMINE-T OR CALCIUM HYPOCHLORITE FOR PRECISION AND ACCURACY TESTS OF THE AT METHOD

Chlorine[a] spiking solution (mg/l)	Volume of solution spiked (ml)	Volume of spiking solution, (µl)	Final concentration of chlorine (µg/l)	Aliquot for dilution (ml)	Volume of deionized water added (ml)	Expected concentration of chlorine (µg/l)
50	200	0	0	None	None	Same
50	200	20	5	None	None	Same
50	200	40	10	None	None	Same
50	200	100	25	None	None	Same
50	200	200	50	None	None	Same
50	200	400	100	None	None	Same
50	200	600	150	None	None	Same
50	200	800	199	None	None	Same
50	200	1000	249	None	None	Same

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[a] Chloramine-T or calcium hypochlorite as chlorine.

TABLE 3. SPIKING EXPERIMENTS WITH 50 % (w/w) MIXTURE OF CHLORAMINE-T AND CALCIUM HYPOCHLORITE AS CHLORINE FOR PRECISION AND ACCURACY TESTS OF THE MC METHOD

Chlorine[a] spiking solution (mg/l)	Volume of solution spiked (ml)	Volume[b] of spiking solution (μl)	Final concentration[b] of chlorine (μg/l)	Aliquot for dilution (ml)	Volume of deionized water added (ml)	Expected concentration of chlorine (μg/l)	Dilution factor
12.5	50	0	0	None	None	None	None
12.5	50	20	10	None	None	Same	None
12.5	50	40	20	None	None	Same	None
12.5	50	100	50	None	None	Same	None
12.5	50	200	99	None	None	Same	None
12.5	50	300	148	20	30	59	2.5
12.5	50	400	197	20	30	79	2.5
12.5	50	500	245	10	40	49	5
12.5	50	1000	481	5	45	48	10

---

[a] Chloramine-T or calcium hypochlorite as chlorine.

[b] Equal volumes of chloramine-T and calcium hypochlorite spiking solutions were added to yield twice the volumes listed. The sum of the two volumes was used in calculating the final concentration.

TABLE 4. SPIKING EXPERIMENTS WITH 50 % (w/w) MIXTURE OF CHLORAMINE-T AND CALCIUM HYPOCHLORITE AS CHLORINE FOR PRECISION AND ACCURACY TESTS OF THE AT METHOD

Chlorine[a] spiking solution (mg/l)	Volume of solution spiked (ml)	Volume[b] of spiking solution, (µl)	Final concentration[b] of chlorine (µg/l)	Aliquot for dilution (ml)	Volume of deionized water added (ml)	Expected concentration of chlorine (µg/l)
50	200	0	0	None	None	Same
50	200	20	10	None	None	Same
50	200	40	20	None	None	Same
50	200	100	50	None	None	Same
50	200	200	100	None	None	Same
50	200	300	150	None	None	Same
50	200	400	199	None	None	Same
50	200	500	249	None	None	Same
50	200	1000	495	None	None	Same

---

[a] Chloramine-T or calcium hypochlorite as chlorine.

[b] Equal volumes of Chloramine-T and calcium hypochlorite spiking solutions were added to yield twice the volumes listed. The sum of the two volumes was used in calculating the final concentration.

TABLE 5. PREPARATION OF SOLUTIONS FOR TESTS OF CHEMICAL INTERFERENCE WITH MC METHOD

Stock spiking solution	Concentration of spiking solution (mg/l)	Volume of spiking solution (μl)	Volume of solution spiked (ml)	Final concentration (μg/l)
Chromium(VI)	50	500	50	500
Mercury(II)	50	10	50	10
Bromide	50	100	50	100
Zinc(II)	100	500	50	990
Copper(II)	50	500	50	500
Iron(III)	1000	500	50	9900
Arsenic(III)	50	500	50	500
Arsenic(III)	50	200	50	200
Arsenic(III)	50	50	50	50
Arsenic(V)	50	50	50	200
Arsenic(V)	50	50	50	50
Manganese(VII)	100	500	50	990

TABLE 6. AT METHOD[a] RECOVERY OF TOTAL CHLORINE FROM DEIONIZED WATER SPIKED WITH 249 μg/1 OF CHLORAMINE-T AS CHLORINE WITH 0.00564N AND 0.001128N PHENYLARSINE OXIDE

Replicate Number	Total Chlorine (μg/1)	Mean	SD[b]	RSD (%)[c]	BIAS (%)
	Experiment 6.1 Titration with 0.00564N (0.20 mg Cl_2/ml) PAO				
1	250	250	0	0	1.2
2	250				
3	250				
	Experiment 6.2 Titration with 0.001128N (0.04 mg Cl_2/ml) PAO				
1	210	209	2.3	1.1	-15.4
2	210				
3	206				

---

[a] AT is forward amperometric titration method.

[b] SD is standard deviation.

[c] % RSD is standard deviation expressed as percentage of mean.

TABLE 7. EXPERIMENTAL RECOVERY BY MC AND AT METHODS OF TOTAL CHLORINE FROM DEIONIZED WATER SPIKED WITH CHLORAMINE-T[a,b]

Replicate Number	Total Chlorine (μg/l)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 7.1 Unspiked, Raw Water[c,d]														
1	-3.5	<20	-1.70		0.95		56.9							
2	-0.9	<20												
3	-2.2	<20												
4	-1.5	<20												
5	-1.5	<20												
6	-0.6	<20												
7	-1.7	<20												
Experiment 7.2 1.25 μg/l Spike[d]														
1	-0.2		0.37		0.36		97.3		-70.4		6.29		YES	
2	0.6													
3	0.6													
4	0.6													
5	0.5													
6	-0.1													
7	0.6													

continued

TABLE 7. CONTINUED

Replicate Number	Total Chlorine (µg/1)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 7.3 2.5 µg/1 Spike[d]														
1	1.8		2.23		0.38		17.0		-10.8		1.88		NO	
2	2.8													
3	1.8													
4	2.4													
5	2.0													
6	2.3													
7	2.5													
Experiment 7.4 5 µg/1 Spike[d]														
1	3.1		3.31		0.30		9.06		-33.8		14.9		YES	
2	3.4													
3	3.2													
4	3.1													
5	3.8													
6	3.6													
7	3.0													

continued

TABLE 7. CONTINUED

Replicate Number	Total Chlorine (μg/1)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
							Experiment 7.5 10 μg/1 Spike[d]							
1	8.2	<20	8.11		0.43		5.30		-18.9		11.6		YES	
2	8.4	<20												
3	7.5	<20												
4	8.4	<20												
5	8.4	<20												
6	7.5	<20												
7	8.4	<20												
							Experiment 7.6 25 μg/1 Spike							
1	24	30	23.9	28.6	0.4	3.8	1.7	13.3	-4.4	14.4	7.3	2.5	YES	YES
2	24	30												
3	24	30												
4	24	20												
5	23	30												
6	24	30												
7	24	30												

continued

TABLE 7. CONTINUED

Replicate Number	Total Chlorine (µg/1)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 7.7 50 µg/1 Spike														
1	49	50	51.3	50	1.4	0	2.7	0	2.6	0	2.5		YES	
2	51	50												
3	53	50												
4	52	50												
5	52	50												
6	52	50												
7	50	50												
Experiment 7.8 100 µg/1 Spike														
1	111	100	109	99	1.6	3.8	1.5	3.8	9.0	-1.0	15	0.7	YES	NO
2	109	100												
3	109	100												
4	109	100												
5	106	100												
6	107	100												
7	109	90												

continued

TABLE 7. CONTINUED

Replicate Number	Total Chlorine (μg/l)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 7.9 247 μg/l Spike														
1	332		304		18.7		6.2		23.1		8.1		YES	
2	297													
3	326													
4	287													
5	303													
6	283													
7	297													
Experiment 7.10 481 μg/l Spike														
1	671		715		126		17.6		48.6		3.7		YES	
2	654													
3	903													
4	632													
5														
6														
7														

continued

TABLE 7. CONTINUED

Replicate Number	Total Chlorine (μg/1)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 7.11 149 μg/1 Spike[e]														
1	152	145	153	148	3.6	3.9	2.4	2.6	2.7	-0.7	2.9	0.7	YES	NO
2	160	150												
3	155	140												
4	152	150												
5	152	150												
6	151	150												
7	149	150												
Experiment 7.12 198 μg/1 Spike[e]														
1	198	190	200	199	4.8	6.1	2.4	3.1	1.0	0.5	1.1	0.4	NO	NO
2	208	200												
3	204	200												
4	198	200												
5	200	210												
6	194	200												
7	196	195												

continued

TABLE 7. CONTINUED

Replicate Number	Total Chlorine (μg/l)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 7.13 247 μg/l Spike[e]														
1	246	230	249	243	1.8	7.6	0.7	3.1	0.8	-1.6	2.9	0.7	YES	NO
2	250	250												
3	248	240												
4	247	240												
5	251	250												
6	250	250												
7	248	240												

---

[a] MC and AT are microprocessor-controlled ion selective electrode and forward amperometric titration methods, respectively. SD is standard deviation, % RSD is standard deviation expressed as percentage of mean, and SAC 95%? is significant at 95% confidence.

[b] Spiked solution was not diluted before analysis by MC to establish linear concentration range.

[c] This solution was background for experiments 7.2-7.13.

[d] An additional significant figure was retained for use in calculating a more precise estimate of minimum detection limit by MC.

[e] Spiked solution was diluted before analysis by MC.

TABLE 8. EFFECTS OF pH, CHEMICAL INTERFERENCE, AND PYROPHOSPHATE (FOR OVERCOMING CHEMICAL INTERFERENCE) ON EXPERIMENTAL RECOVERY BY MC METHOD OF TOTAL CHLORINE FROM DEIONIZED WATER SPIKED WITH 50 μg/l OF CHLORAMINE-T AS CHLORINE[a]

Replicate Number	Total Chlorine (μg/1)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
Experiment 8.1. pH 3.6 Buffer							
1	52	51.7	1.6	3.1	3.4	2.8	YES
2	53						
3	51						
4	51						
5	54						
6	52						
7	49						
Experiment 8.2 pH 3.8 Buffer							
1	52	52.6	0.8	1.5	5.2	8.6	YES
2	52						
3	52						
4	53						
5	52						
6	53						
7	54						
Experiment 8.3 pH 4.0 Buffer							
1	49	51.9	2.3	4.4	3.8	2.2	NO
2	52						
3	55						
4	51						
5	51						
6	55						
7	50						

continued

TABLE 8. CONTINUED

Replicate Number	Total Chlorine (μg/l)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
Experiment 8.4 pH 4.2 Buffer							
1	50	52.0	2.2	4.2	4.0	2.4	YES
2	52						
3	51						
4	50						
5	54						
6	51						
7	56						
Experiment 8.5 pH 4.4 Buffer							
1	51	52.0	1.7	3.3	4.0	3.1	YES
2	53						
3	51						
4	51						
5	55						
6	50						
7	53						
Experiment 8.6 500 μg/l of Chromium(VI)							
1	46	47.6	2.8	5.9	-4.8	2.3	NO
2	48						
3	53						
4	47						
5	47						
6	48						
7	44						

continued

TABLE 8. CONTINUED

Replicate Number	Total Chlorine (μg/1)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
Experiment 8.7 10 μg/1 of Mercury							
1	48	50.0	1.7	3.4	0	0	NO
2	52						
3	49						
4	52						
5	50						
6	48						
7	51						
Experiment 8.8 100 μg/1 of Bromide							
1	48	48.9	0.4	0.8	-2.2	7.3	YES
2	49						
3	49						
4	49						
5	49						
6	49						
7	49						
Experiment 8.9 990 μg/1 Zinc(II)							
1	52	51.3	2.0	3.9	2.6	1.7	NO
2	50						
3	51						
4	52						
5	50						
6	49						
7	55						

continued

TABLE 8. CONTINUED

Replicate Number	Total Chlorine (µg/1)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
Experiment 8.10 1000 µg/1 of Zinc(II)							
1	137	132	16.2	12.3	164	13	YES
2	154						
3	111						
4	113						
5	144						
6	140						
7	124						
Experiment 8.11 10 mg/1 of Zinc(II)							
1	54	56.8	2.1	3.7	13.6	8.6	YES
2	59						
3	57						
4	57						
5							
6							
7							
Experiment 8.12 10 mg/1 of Zinc(II) with 2 % (w/v) Sodium Pyrophosphate Decahydrate							
1	48	50.0	1.3	2.6	0	0	NO
2	52						
3	50						
4	50						
5	51						
6	49						
7	50						

continued

TABLE 8. CONTINUED

Replicate Number	Total Chlorine (μg/l)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
		Experiment 8.13 500 μg/l of Copper(II)					
1	52	53.4	2.7	5.1	6.8	3.3	YES
2	51						
3	58						
4	56						
5	52						
6	54						
7	51						
		Experiment 8.14 500 mg/l of Copper(II)					
1	84	117	35	30	134	5.1	YES
2	163						
3	146						
4	148						
5	80						
6	83						
7	116						
		Experiment 8.15 5 mg/l Copper(II)					
1	63	67.0	2.7	4.0	34	17	YES
2	68						
3	69						
4	68						
5							
6							
7							

continued

TABLE 8. CONTINUED

Replicate Number	Total Chlorine (µg/l)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
Experiment 8.16 5 mg/l of Copper(II) With 2 % (w/v) Sodium Pyrophosphate Decahydrate							
1	49	48.7	0.5	1.0	-2.6	6.9	YES
2	48						
3	49						
4	49						
5	49						
6	49						
7	48						
Experiment 8.17 1000 mg/l of Iron(III)							
1	987	1389	322	23.2	2680	11	YES
2	1203						
3	1828						
4	1370						
5	1699						
6	1568						
7	1068						
Experiment 8.18 1000 mg/l of Iron(III) With 2 % (w/v) Sodium Pyrophosphate Decahydrate							
1	56	55.9	7.3	13.1	11.8	2.1	NO
2	67						
3	62						
4	54						
5	44						
6	52						
7	56						

continued

TABLE 8. CONTINUED

Replicate Number	Total Chlorine (μg/l)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
Experiment 8.19 9900 μg/l of Iron(III)							
1	68	62.3	2.9	4.7	24.6	11	YES
2	60						
3	60						
4	62						
5	60						
6	62						
7	64						
Experiment 8.20 9900 μg/l of Iron(III) With 2 % (w/v) Sodium Pyrophosphate Decahydrate							
1	46	49.1	1.7	3.5	-1.8	1.4	NO
2	50						
3	48						
4	50						
5	50						
6	49						
7	51						
Experiment 8.21 5 mg/l of Iron(III)							
1	56	54	1.3	2.4	8	8.1	YES
2	55						
3	54						
4	52						
5	53						
6	53						
7	54						

continued

TABLE 8. CONTINUED

Replicate Number	Total Chlorine (μg/l)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
Experiment 8.22 500 μg/l of Arsenic(III)							
1	196	119	114	96	138	1.6	NO
2	246						
3	-21						
4	7						
5	193						
6	12						
7	199						
Experiment 8.23 200 μg/l of Arsenic(III)							
1	74	75.1	5.2	6.9	50	13	YES
2	65						
3	77						
4	74						
5	78						
6	76						
7	82						
Experiment 8.24 50 μg/l of Arsenic(III)							
1	40	43.6	3.3	7.6	-12.8	5.1	YES
2	41						
3	43						
4	48						
5	48						
6	44						
7	41						

continued

TABLE 8. CONTINUED

Replicate Number	Total Chlorine (μg/l)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
Experiment 8.25 200 μg/l of Arsenic(V)							
1	50	49.4	2.5	5.1	-1.2	0.6	NO
2	51						
3	48						
4	53						
5	47						
6	51						
7	46						
Experiment 8.26 50 μg/l of Arsenic(V)							
1	46	48.6	1.9	3.9	-2.8	2.0	NO
2	49						
3	49						
4	46						
5	49						
6	51						
7	50						
Experiment 8.27 990 μg/l of Manganese(VII)							
1	1290	-1867	2741	147	-3834	1.2	NO
2	-3250						
3	-3640						
4							
5							
6							
7							

---

[a] MC is microprocessor-controlled ion selective electrode method, SD is standard deviation, % RSD is standard deviation expressed as percentage of mean, and SAC 95%? is significant at 95% confidence.

TABLE 9. EFFECT OF 2 % (w/v) SODIUM PYROPHOSPHATE FOR OVERCOMING CHEMICAL INTERFERENCE ON EXPERIMENTAL RECOVERY BY MC METHOD OF TOTAL CHLORINE FROM DEIONIZED WATER SPIKED WITH CHLORAMINE-T AS CHLORINE[a]

Replicate Number	Total Chlorine (µg/l)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
Experiment 9.1 Unspiked, Raw Water[b]							
1	-5	-5.4	1.1	20.4			
2	-6						
3	-6						
4	-6						
5	-7						
6	-4						
7	-4						
Experiment 9.2 5 µg/l Spike							
1	2	-0.9	2.2	244	-118		
2	2						
3	-2						
4	-2						
5	0						
6	-3						
7	-3						
Experiment 9.3 10 µg/l Spike							
1	4	4.6	2.6	56.5	-54	5.5	YES
2	5						
3	-1						
4	6						
5	6						
6	6						
7	6						

continued

TABLE 9. CONTINUED

Replicate Number	Total Chlorine (μg/1)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
Experiment 9.4 25 μg/1 Spike							
1	21	21.6	1.3	6.0	-13.6	6.9	YES
2	22						
3	22						
4	20						
5	24						
6	21						
7	21						
Experiment 9.5 50 μg/1 Spike							
1	44	44.9	0.9	2.0	-10.2	15	YES
2	45						
3	46						
4	45						
5	44						
6	44						
7	46						
Experiment 9.6 100 μg/1 Spike							
1	88	92.7	6.1	6.6	-7.3	3.2	YES
2	91						
3	86						
4	105						
5	93						
6	92						
7	94						

continued

TABLE 9. CONTINUED

Replicate Number	Total Chlorine (μg/l)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
		Experiment 9.7 149 μg/l Spike					
1	124	136	13.2	9.7	-8.7	2.6	YES
2	123						
3	137						
4	154						
5	135						
6	127						
7	154						
		Experiment 9.8 198 μg/l Spike					
1	160	171	8.5	5.0	-13.6	8.4	YES
2	174						
3	158						
4	179						
5	172						
6	174						
7	179						
		Experiment 9.9 247 μg/l Spike					
1	223	222	10.7	4.8	-10	6.2	YES
2	240						
3	213						
4	212						
5	227						
6	211						
7	228						

---

[a] MC is microprocessor-controlled ion selective electrode method, SD is standard deviation, % RSD is standard deviation expressed as percentage of mean, and SAC 95%? is significant at 95% confidence.

[b] This solution was background for experiments 9.2-9.9.

TABLE 10. EFFECT OF 2 % (w/v) SODIUM PYROPHOSPHATE FOR OVERCOMING CHEMICAL INTERFERENCE ON EXPERIMENTAL RECOVERY BY MC METHOD OF TOTAL CHLORINE FROM DEIONIZED WATER SPIKED WITH CALCIUM HYPOCHLORITE AS CHLORINE[a]

Replicate Number	Total Chlorine (μg/l)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
Experiment 10.1 Unspiked, Raw Water[b]							
1	-4	-4.3	1.0	23.3			
2	-4						
3	-4						
4	-4						
5	-6						
6	-5						
7	-3						
Experiment 10.2 5 μg/l Spike							
1	1	1	0	0	-80		
2	1						
3	1						
4	1						
5	1						
6	1						
7	1						
Experiment 10.3 10 μg/l Spike							
1	7	5.7	0.8	14.0	-43	14	YES
2	6						
3	6						
4	6						
5	5						
6	5						
7	5						

continued

TABLE 10. CONTINUED

Replicate Number	Total Chlorine (μg/l)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
		Experiment 10.4 25 μg/l Spike					
1	20	18.4	1.4	7.6	-26	12	YES
2	20						
3	18						
4	19						
5	18						
6	18						
7	16						
		Experiment 10.5 50 μg/l Spike					
1	42	44.1	4.0	9.1	-11.8	3.9	YES
2	41						
3	40						
4	41						
5	49						
6	48						
7	48						
		Experiment 10.6 100 μg/l Spike					
1	96	92.9	3.0	3.2	-7.1	6.3	YES
2	91						
3	98						
4	92						
5	91						
6	90						
7	92						

continued

TABLE 10. CONTINUED

Replicate Number	Total Chlorine (μg/l)	Mean	SD	RSD (%)	Bias (%)	t Value	SAC 95%?
		Experiment 10.7 149 μg/l Spike					
1	81	78	15.5	19.9	-48	12	YES
2	68						
3	107						
4	63						
5	87						
6	71						
7	66						
		Experiment 10.8 198 μg/l Spike					
1	117	107	12.7	11.9	-46	19	YES
2	100						
3	100						
4	109						
5	128						
6	108						
7	89						

---

[a] MC is microprocessor-controlled ion selective electrode method, SD is standard deviation, % RSD is standard deviation expressed as percentage of mean, and SAC 95%? is significant at 95% confidence.

[b] This solution was background for experiments 10.2-10.8.

TABLE 11. EXPERIMENTAL RECOVERY BY MC AND AT METHODS OF TOTAL CHLORINE FROM DEIONIZED WATER SPIKED WITH CALCIUM HYPOCHLORITE AS CHLORINE[a]

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
					Experiment 11.1 Unspiked, Raw Water[b,c]									
1	-0.7	<20	-1.61		1.27		78.9							
2	0.0	<20												
3	-1.2	<20												
4	-1.4	<20												
5	-1.6	<20												
6	-3.9	<20												
7	-2.5	<20												
					Experiment 11.2 5 µg/l Spike[c]									
1	3.6	<20	3.66		0.51		13.9		-26.8		6.95		YES	
2	3.9	<20												
3	3.5	<20												
4	4.6	<20												
5	3.7	<20												
6	3.0	<20												
7	3.3	<20												

continued

TABLE 11. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 11.3 10 µg/l Spike[c,d]														
1	7.9	<20	7.91	11.4	0.45	3.8	5.69	33.3	-20.9	14.0	12.3	1.0	YES	
2	8.3	20												
3	8.1	<20												
4	7.6	<20												
5	7.6	<20												
6	7.3	<20												
7	8.6	<20												
Experiment 11.4 25 µg/l Spike														
1	22	20	22.4	26.4	2.0	4.8	8.9	18.2	-10.4	5.6	3.4	0.2	YES	
2	23	30												
3	21	20												
4	21	25												
5	20	30												
6	25	30												
7	25	30												

continued

TABLE 11. CONTINUED

Replicate Number	Total Chlorine (μg/l)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 11.5 50 μg/l Spike														
1	49	50	49.3	49.3	1.4	1.9	2.8	3.9	-1.4	-1.4	1.3	1.0	NO	NO
2	50	50												
3	50	50												
4	47	50												
5	48	45												
6	51	50												
7	50	50												
Experiment 11.6 100 μg/l Spike														
1	109	90	109	91	2.2	3.8	2.0	4.2	9.0	-9.0	11	6.3	YES	YES
2	111	90												
3	110	90												
4	109	90												
5	104	90												
6	109	100												
7	108	90												

continued

TABLE 11. CONTINUED

Replicate Number	Total Chlorine (μg/1)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 11.7 149 μg/1 Spike														
1	162	150	147	148	9.2	3.9	6.3	2.6	-1.3	-0.7	0.6	0.7	NO	NO
2	150	150												
3	149	150												
4	131	140												
5	144	150												
6	144	150												
7	146	145												
Experiment 11.8 198 μg/1 Spike														
1	201	190	196	199	3.7	6.1	1.9	3.1	-1.0	0.5	1.4	0.4	NO	NO
2	199	200												
3	200	200												
4	193	210												
5	192	200												
6	193	200												
7	197	195												

continued

TABLE 11. CONTINUED

Replicate Number	Total Chlorine (μg/1)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 11.9 247 μg/1 Spike														
1	244	230	230	243	4.2	7.0	1.8	2.9	-6.9	-1.6	28	1.5	YES	NO
2	234	245												
3	232	250												
4	232	240												
5	224	240												
6	231	250												
7	233	245												

---

[a] MC and AT are microprocessor-controlled ion selective electrode and forward amperometric titration methods, respectively. SD is standard deviation, % RSD is standard deviation expressed as percentage of mean, and SAC 95%? is significant at 95% confidence.

[b] This solution was background for experiments 11.2-11.9.

[c] An additional significant figure was retained for use in calculating a precise estimate of minimum detection limit by MC.

[d] For the AT, results less than 20 μg/1 were included in the statistical calculations as 10 μg/1.

TABLE 12. EXPERIMENTAL RECOVERY BY MC AND AT METHODS OF TOTAL CHLORINE FROM DEIONIZED WATER SPIKED WITH 50 % (w/w) MIXTURE OF CALCIUM HYPOCHLORITE AND CHLORAMINE-T AS CHLORINE[a]

Replicate Number	Total Chlorine (μg/l)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 12.1 Unspiked, Raw Water[b,c]														
1	-1.6	<20	-2.51		1.30		51.8							
2	-5.3	<20												
3	-1.8	<20												
4	-2.3	<20												
5	-1.6	<20												
6	-2.3	<20												
7	-2.7	<20												
Experiment 12.2 10 μg/l Spike[c]														
1	9.8	<20	9.10		0.42		4.61		-9.00		5.67		YES	
2	9.3	<20												
3	8.9	<20												
4	9.0	<20												
5	8.7	<20												
6	8.6	<20												
7	9.4	<20												

continued

TABLE 12. CONTINUED

Replicate Number	Total Chlorine (μg/l)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
						Experiment 12.3 20 μg/l Spike[d]								
1	21	<20	19.6	14.3	1.0	5.3	5.1	37.1	-2.0	-28.5	2.6	2.9	YES	YES
2	20	<20												
3	18	<20												
4	19	20												
5	20	20												
6	20	20												
7	19	<20												
						Experiment 12.4 50 μg/l Spike								
1	50	50	49.3	49.0	1.1	2.4	2.2	4.9	-1.4	-2.0	1.7	1.1	NO	NO
2	50	45												
3	51	50												
4	49	50												
5	48	50												
6	49	45												
7	48	50												

continued

TABLE 12. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 12.5 100 µg/l Spike														
1	105	100	102	99	3.9	1.9	3.8	1.9	2.0	-1.0	1.4	1.4	NO	NO
2	105	100												
3	105	100												
4	105	100												
5	99	95												
6	99	100												
7	96	100												
Experiment 12.6 149 µg/l Spike														
1	148	150	136	150	16.8	5.0	12.4	3.3	-8.7	0.7	2.0	0.5	NO	NO
2	152	150												
3	131	155												
4	153	140												
5	129	150												
6	106	150												
7	131	155												

continued

TABLE 12. CONTINUED

Replicate Number	Total Chlorine (µg/1)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 12.7 198 µg/1 Spike														
1	209	210	202	202	5.9	8.1	2.9	4.0	2.0	2.0	1.8	1.3	NO	NO
2	204	210												
3	207	200												
4	208	210												
5	197	195												
6	196	190												
7	196	200												
Experiment 12.8 247 µg/1 Spike														
1	245	250	247	249	5.0	6.9	2.0	2.8	0	0.8	0	0.8	NO	NO
2	251	240												
3	247	250												
4	247	250												
5	238	260												
6	254	250												
7	246	240												

continued

TABLE 12. CONTINUED

Replicate Number	Total Chlorine (µg/1)		Mean		SD		RSD (%)		Bias (%)		t Value		SAC 95%?	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 12.9 488 µg/1 Spike														
1	459	430	467	451	19.4	10.2	4.2	2.3	-4.3	-7.6	2.9	9.6	YES	YES
2	443	450												
3	482	450												
4	491	460												
5	442	450												
6	469	455												
7	481	460												

---

[a] MC and AT are microprocessor-controlled ion selective electrode and forward amperometric titration methods, respectively. SD is standard deviation, % RSD is standard deviation expressed as percentage of mean, and SAC 95%? is significant at 95% confidence.

[b] This solution was background for experiments 12.2-12.9.

[c] An additional significant figure was retained for use in calculating a precise estimate of minimum detection limit by MC.

[d] For the AT, results less than 20 µg/1 were included in the statistical calculations as 10 µg/1.

TABLE 13. CHLORINE DEMAND OF RAW ROSS LANDING SURFACE RIVER WATER SAMPLE COLLECTED OCTOBER 3, 1980[a]

Contact Time (Min)	Chlorine Concentration, mg/l		
	Added	Found	Demand[b]
1	0.2	0.22	-0.02
1	0.6	0.52	0.08
1	1.0	0.92	0.08
1	3.0	2.5	0.5
1	5.0	4.4	0.6
5	0.2	0.22	-0.02
5	0.6	0.58	0.02
5	1.0	0.68	0.32
5	3.0	1.6	1.4
5	5.0	2.6	2.4
10	0.2	0.22	-0.02
10	0.6	0.50	0.1
10	1.0	0.70	0.3
10	3.0	1.3	1.7
10	5.0	2.7	2.3
15	0.2	0.22	-0.02
15	0.6	0.50	0.1
15	1.0	0.65	0.35
15	3.0	1.4	1.6
15	5.0	2.2	2.8
30	0.2	0.20	0.0
30	0.6	0.48	0.12
30	1.0	0.65	0.35
30	3.0	1.2	1.8
30	5.0	2.8	2.2
60	1.2	0.20	0.0
60	0.6	0.44	0.16
60	1.0	0.72	0.28
60	3.0	1.4	1.6
60	5.0	3.2	1.8

---

[a] Ross Landing is located on the Tennessee River in Chattanooga, Tennessee.

[b] Demand is difference between total chlorine added initially as NaOCl-Cl_2 and that found after elapsed contact time.

TABLE 14. INORGANIC SPECIES CONCENTRATIONS, SANITARY CHEMICAL CHARACTERISTICS, AND PHYSICAL PROPERTIES OF TENNESSEE RIVER WATER COLLECTED AT ROSS LANDING, CHATTANOOGA, TENNESSEE, OCTOBER 3, 1980

Characteristics	Value
Inorganics, μg/l	
Arsenic	< 2
Chromium	< 1
Copper	< 10
Iron	190
Mercury	< 0.2
Manganese	30
Zinc	< 10
Solids, mg/l	
Suspended	3
Dissolved	110
Chemical oxygen demand, mg/l	8
Total organic carbon mg/l	2.6
Nitrogen, mg/l as N	
Organic	
Nitrite plus nitrate	0.34
Ammonia	< 0.01
Alkalinity, mg/l as $CaCO_3$	
Total	64
Phenol	< 1
Color, mg/l of Pt in the chloroplatinate standard	
True	4
Apparent	13
Turbidity, mg/l of natural Si	7.1
pH	7

TABLE 15. EXPERIMENTAL RECOVERY BY MC AND AT METHODS OF TOTAL CHLORINE FROM RAW ROSS LANDING SURFACE RIVER WATER SAMPLE COLLECTED OCTOBER 3, 1980, SPIKED WITH CHLORAMINE-T[a]

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 15.1 Unspiked, Raw Water[b]										
1	-9	<20	-7.9		1.5		19.0			
2	-8	<20								
3	-7	<20								
4	-8	<20								
5	-5	<20								
6	-9	<20								
7	-9	<20								
Experiment 15.2[c] Analyzed October 12, 1980[c]										
1	26	<20	28.0	11.4	1.3	3.8	4.6	33.3	50	50
2	28	<20								
3	27	<20								
4	28	20								
5	30	<20								
6	28	<20								
7	29	<20								
Experiment 15.3 Analyzed October 8, 1980										
1	34	<20	33.3		1.1		3.3		55	55
2	33	<20								
3	33	<20								
4	35	<20								
5	34	<20								
6	32	<20								
7	32	<20								

continued

TABLE 15. CONTINUED

Replicate Number	Total Chlorine (μg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (μg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
	Experiment 15.4[c] Analyzed October 7, 1980[c]									
1	36	<20	36.0	15.7	0.8	5.3	2.2	33.8	60	60
2	37	20								
3	35	20								
4	36	20								
5	37	20								
6	35	<20								
7	36	<20								
	Experiment 15.5 Analyzed October 7, 1980									
1	48	30	48.6	28.6	0.5	4.8	1.0	16.8	75	75
2	49	30								
3	49	20								
4	48	30								
5	49	25								
6	48	35								
7	49	30								
	Experiment 15.6 Analyzed October 7, 1980									
1	70	60	70.7	55.0	0.8	5.0	1.1	9.1	99	100
2	72	50								
3	71	50								
4	71	60								
5	70	60								
6	70	50								
7	71	55								

continued

TABLE 15. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 15.7 Analyzed October 7, 1980										
1	120	100	118	101	3.0	3.8	2.5	3.8	148	150
2	121	100								
3	112	110								
4	118	100								
5	118	100								
6	119	100								
7	120	100								
Experiment 15.8 Analyzed October 7, 1980										
1	178	150	171	149	4.9	1.9	2.9	1.3	197	199
2	178	150								
3	168	150								
4	168	150								
5	167	145								
6	170	150								
7	168	150								
Experiment 15.9 Analyzed October 3, 1980										
1	208	200	206	201	5.9	4.5	2.9	2.2	245	249
2	208	200								
3	212	200								
4	210	195								
5	200	200								
6	196	210								
7	210	200								

continued

TABLE 15. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 15.10 Analyzed October 7, 1980										
1	203	200	210	199	8.2	2.4	3.9	1.2	245	249
2	221	200								
3	221	200								
4	205	195								
5	202	200								
6	212	200								
7	206	195								
Experiment 15.11 Analyzed October 7, 1980										
1	240	240	255	248	7.9	7.0	3.1	2.8	295	299
2	264	250								
3	258	250								
4	252	240								
5	259	260								
6	260	250								
7	252	245								

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[a] Ross Landing is located on the Tennessee River in Chattanooga, Tennessee. MC and AT are microprocessor-controlled ion selective electrode and forward amperometric titration methods, respectively. SD is standard deviation, % RSD is standard deviation expressed as percentage of mean, and SAC 95%? is significant at 95% confidence.

[b] This solution was background for experiments 15.2-15.11.

[c] For the AT, results less than 20 µg/l were included in the statistical calculations as 10 µg/l.

TABLE 16. EXPERIMENTAL RECOVERY BY MC AND AT METHODS OF TOTAL CHLORINE FROM RAW ROSS LANDING SURFACE RIVER WATER SAMPLE COLLECTED OCTOBER 3, 1980, SPIKED WITH CALCIUM HYPOCHLORITE[a,b]

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 16.1 Analyzed October 12, 1980[c]										
1	-1.8	<20	0.0857		1.14		1330		15	25
2	-0.6	<20								
3	1.3	<20								
4	1.2	<20								
5	-0.1	<20								
6	-0.4	<20								
7	1.0	<20								
Experiment 16.2 Analyzed October 12, 1980[c]										
1	10.3	<20	9.59		0.46		4.80		30	50
2	9.8	<20								
3	9.4	<20								
4	10.0	<20								
5	9.1	<20								
6	9.1	<20								
7	9.4	<20								
Experiment 16.3 Analyzed October 12, 1980										
1	25	30	26.3	28.6	0.8	2.4	3.1	8.3	55	90
2	26	30								
3	27	30								
4	26	25								
5	26	30								
6	27	30								
7	27	25								

continued

TABLE 16. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 16.4 Analyzed October 12, 1980										
1	52	50	52.4	45.7	1.6	4.5	3.1	9.8	80	125
2	55	45								
3	50	50								
4	52	40								
5	52	40								
6	54	50								
7	52	45								
Experiment 16.5 Analyzed October 12, 1980										
1	92	100	92.4	97.1	0.8	3.9	0.9	4.0	129	180
2	94	90								
3	92	95								
4	92	100								
5	92	100								
6	93	95								
7	92	100								
Experiment 16.6 Analyzed October 12, 1980										
1	150	150	145	149	4.1	1.9	2.8	1.3	202	249
2	148	145								
3	141	150								
4	141	150								
5	140	150								
6	147	150								
7	147	150								

continued

TABLE 16. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 16.7 Analyzed October 12, 1980										
1	200	180	196	190	2.5	5.0	1.3	2.6	344	304
2	194	190								
3	195	190								
4	196	195								
5	194	190								
6	199	195								
7	194	190								
Experiment 16.8 Analyzed October 12, 1980										
1	232	250	229	250	9.9	0	4.3	0	383	434
2	231	250								
3	232	250								
4	232	250								
5	230	250								
6	208	250								
7	240	250								

---

[a] Ross Landing is located in Chattanooga Tennessee. MC and AT are microprocessor-controlled ion selective electrode and forward amperometric titration methods, respectively. SD is standard deviation and % RSD is standard deviation expressed as percentage of mean.

[b] Background for experiments 16.1-16.6 is shown by experiment 15.1, Table 15.

[c] An additional significant figure was retained for use in calculating a precise estimate of minimum detection limit by MC.

TABLE 17. CHLORINE DEMAND OF RAW KINGSTON STEAM PLANT SAMPLE COMPOSED OF 100 % (v/v) UNCHLORINATED RAW RIVER WATER INTAKE AT WATER SUPPLY PLANT, COLLECTED OCTOBER 15, 1980[a]

Contact Time (Min)	Chlorine Concentration, mg/l		
	Added	Found	Demand[b]
1	0.2	0.20	0.00
1	0.6	0.70	-0.1
1	1.0	1.0	0.00
1	3.0	2.6	0.4
1	5.0	4.9	0.1
5	0.2	0.2	0.00
5	0.6	0.6	0.00
5	1.0	0.96	0.04
5	3.0	2.4	0.6
5	5.0	3.5	1.5
10	0.2	0.2	0.00
10	0.6	0.5	0.1
10	1.0	0.84	0.16
10	3.0	2.4	0.6
10	5.0	3.4	1.6
15	0.2	0.2	0.00
15	0.6	0.46	0.14
15	1.0	0.8	0.2
15	3.0	2.3	0.7
15	5.0	3.5	1.5
30	0.2	0.2	0.00
30	0.6	0.42	0.18
30	1.0	0.78	0.22
30	3.0	2.0	1.0
30	5.0	3.4	1.6
60	0.2	0.2	0.00
60	0.6	0.4	0.2
60	1.0	0.6	0.4
60	3.0	1.9	1.1
60	5.0	3.4	1.6

---

[a] Kingston Steam Plant is located near Kingston, Tennessee.

[b] Demand is difference between total chlorine added initially as $NaOCl\text{-}Cl_2$ and that found after elapsed contact time.

TABLE 18. INORGANIC SPECIES CONCENTRATIONS, SANITARY CHEMICAL CHARACTERISTICS, AND PHYSICAL PROPERTIES OF RAW KINGSTON STEAM PLANT SAMPLE COMPOSED OF 100 % (v/v) UNCHLORINATED RAW RIVER WATER INTAKE AT WATER SUPPLY PLANT COLLECTED OCTOBER 15, 1980[a]

Characteristics	Value
Inorganics, µg/l	
Arsenic	6
Chromium	< 1
Copper	120
Iron	890
Mercury	< 0.2
Manganese	50
Zinc	10
Solids, mg/l	
Suspended	9
Dissolved	140
Chemical oxygen demand, mg/l	3
Total organic carbon mg/l	1.8
Nitrogen, mg/l as N	
Organic	0.16
Nitrite plus nitrate	0.30
Ammonia	< 0.01
Alkalinity, mg/l as $CaCO_3$	
Total	85
Phenol	0
Color, mg/l of Pt in the chloroplatinate standard	
True	4
Apparent	15
Turbidity, mg/l of natural Si	6.0
pH	7.0

---

[a] The Kingston Steam Plant is located near Kingston, Tennessee.

TABLE 19. EXPERIMENTAL RECOVERY BY MC AND AT METHODS OF TOTAL CHLORINE FROM UNSPIKED, CHLORINATED KINGSTON STEAM PLANT CONDENSER COOLING RIVER WATER SAMPLES AND ONES SPIKED WITH CALCIUM HYPOCHLORITE[a]

Replicate Number	Total Chlorine (µg/l) MC	Total Chlorine (µg/l) AT	Mean MC	Mean AT	SD MC	SD AT	RSD (%) MC	RSD (%) AT	Total Chlorine Spike (µg/l) MC	Total Chlorine Spike (µg/l) AT
Experiment 19.1 Unspiked Sample Composed of 100 % (v/v) Unchlorinated Raw River Water Intake at Water Supply Plant, Collected and Analyzed October 15, 1980[b]										
1	5.3	<20	4.27		0.63		14.8			
2	4.0	<20								
3	3.4	<20								
4	4.3	<20								
5	4.3	<20								
6	4.8	<20								
7	3.8	<20								
Experiment 19.2 Unspiked Sample Composed of 75 % (v/v) Unchlorinated Raw River Water Intake at Water Supply Plant and 25 % (v/v) Chlorinated Unit Number 2 Condenser Discharge at Plant Outlet, Collected, Composited, and Analyzed October 15, 1980										
1	15	<20	15.0		1.0		6.7			
2	15	<20								
3	15	<20								
4	17	<20								
5	15	<20								
6	14	<20								
7	14	<20								
Experiment 19.3 Spiked Sample Shown in Experiment 19.2[c]										
1	11	<20	11.3		1.0		8.8		25	15
2	11	<20								
3	11	<20								
4	10	<20								
5	12	<20								
6	13	<20								
7	11	<20								

continued

TABLE 19. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 19.4 Unspiked Sample Composed of 50 % (v/v) Unchlorinated Raw River Water Intake at Water Supply Plant and 50 % (v/v) Chlorinated Unit Number 2 Condenser Discharge at Plant Outlet Collected, Composited, and Analyzed October 15, 1980										
1	28	30	27.0	27.9	1.7	3.9	6.3	14.0		
2	24	30								
3	29	25								
4	26	20								
5	28	30								
6	26	30								
7	28	30								
Experiment 19.5 Spiked Sample Shown in Experiment 19.4[c]										
1	20	20	21.3	22.9	1.7	2.7	8.0	11.8	40	50
2	24	25								
3	20	20								
4	20	25								
5	23	25								
6	20	25								
7	22	20								
Experiment 19.6 Unspiked Sample Composed of 100 % (v/v) Chlorinated Unit Number 2 Condenser Discharge at Plant Outlet, Collected and Analyzed October 15, 1980										
1	56	60	53.6	51.4	2.4	7.5	4.5	14.6		
2	57	60								
3	54	55								
4	52	40								
5	53	50								
6	50	45								
7	53	50								

continued

TABLE 19. CONTINUED

Replicate Number	Total Chlorine (µg/l) MC	Total Chlorine (µg/l) AT	Mean MC	Mean AT	SD MC	SD AT	RSD (%) MC	RSD (%) AT	Total Chlorine Spike (µg/l) MC	Total Chlorine Spike (µg/l) AT
Experiment 19.7 Spiked Sample Shown in Experiment 19.6[c]										
1	44	75	44.1	70.0	4.5	5.0	10.2	7.1	60	115
2	48	75								
3	50	70								
4	45	70								
5	43	70								
6	36	70								
7	43	60								
Experiment 19.8 Unspiked Sample Composed of 100 % (v/v) Chlorinated Unit Number 2 Condenser Discharge Outlet Water, Collected and Analyzed October 16, 1980										
1	107	120	105	125	5.0	8.7	4.8	7.0		
2	114	130								
3	104	130								
4	108	110								
5	102	135								
6	102	120								
7	99	130								
Experiment 19.9 Spiked Sample Shown in Experiment 19.8[c]										
1	111	85	91.4	82.1	14.0	7.0	15.3	8.5	99	100
2	94	85								
3	99	85								
4	97	75								
5	93	70								
6	76	85								
7	70	90								

continued

TABLE 19. CONTINUED

Replicate Number	Total Chlorine (µg/l) MC	Total Chlorine (µg/l) AT	Mean MC	Mean AT	SD MC	SD AT	RSD (%) MC	RSD (%) AT	Total Chlorine Spike (µg/l) MC	Total Chlorine Spike (µg/l) AT
Experiment 19.10 Unspiked Sample Composed of 100 % (v/v) Chlorinated Unit Number 2 Condenser Discharge Outlet, Collected and Analyzed October 16, 1980										
1	176	170	178	173	7.8	3.9	4.4	2.3		
2	180	170								
3	186	175								
4	177	170								
5	174	175								
6	164	170								
7	187	180								
Experiment 19.11 Spiked Sample Shown in Experiment 19.10[c]										
1	165	180	160	171	10.9	6.3	6.8	3.7	197	199
2	179	165								
3	164	175								
4	162	165								
5	148	175								
6	148	175								
7	156	165								

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[a] The Kingston Steam Plant is located near Kingston, Tennessee; MC and AT are microprocessor-controlled ion selective electrode and forward amperometric titration methods, respectively; SD is standard deviation, and % RSD is standard deviation expressed as percentage of mean.

[b] An additional significant figure was retained for use in calculating a precise estimate of minimum detection limit by the MC method.

[c] Total chlorine is the value obtained by subtracting the mean background concentration of the unspiked sample.

TABLE 20. CHLORINE DEMAND OF RAW SHAWNEE STEAM PLANT SAMPLE COMPOSED OF 100 % (v/v) UNCHLORINATED UNIT NUMBER 5 CONDENSER DISCHARGE OUTLET WATER, COLLECTED OCTOBER 21, 1980[a]

Contact Time (Min)	Chlorine Concentration, mg/l		
	Added	Found	Demand[b]
1	0.2	0.20	0.0
1	0.6	0.48	0.12
1	1.0	0.86	0.14
1	3.0	2.8	0.2
1	5.0	4.8	0.2
5	0.2	0.20	0.0
5	0.6	0.48	0.12
5	1.0	0.82	0.18
5	3.0	2.2	0.8
5	5.0	4.6	0.4
10	0.2	0.20	0.0
10	0.6	0.48	0.12
10	1.0	0.70	0.3
10	3.0	2.2	0.8
10	5.0	4.4	0.6
15	0.2	0.20	0.0
15	0.6	0.48	0.12
15	1.0	0.66	0.34
15	3.0	1.9	1.1
15	5.0	4.2	0.8
30	0.2	0.20	0.0
30	0.6	0.42	0.18
30	1.0	0.58	0.42
30	3.0	1.8	1.2
30	5.0	4.1	0.9
60	0.2	0.20	0.0
60	0.6	0.40	0.2
60	1.0	0.56	0.44
60	3.0	1.2	1.8
60	5.0	3.7	1.3

---

[a] Shawnee Steam Plant is located near Paducah, Kentucky.

[b] Demand is difference between total chlorine added initially as NaOCl-Cl_2 and that found after elapsed contact time.

TABLE 21. INORGANIC SPECIES CONCENTRATIONS, SANITARY CHEMICAL CHARACTERISTICS, AND PHYSICAL PROPERTIES OF RAW SHAWNEE STEAM PLANT SAMPLE COMPOSED OF 100 % (v/v) UNCHLORINATED UNIT NUMBER 5 CONDENSER DISCHARGE OUTLET WATER, COLLECTED OCTOBER 21, 1980[a]

Characteristics	Value
Inorganics, μg/l	
Arsenic	2
Chromium	< 1
Copper	10
Iron	1200
Mercury	0.3
Manganese	150
Zinc	20
Solids, mg/l	
Suspended	37
Dissolved	220
Chemical oxygen demand, mg/l	10
Total organic carbon mg/l	4.4
Nitrogen, mg/l as N	
Organic	0.26
Nitrite plus nitrate	0.59
Ammonia	0.06
Alkalinity, mg/l as $CaCO_3$	
Total	91
Phenol	< 1
Color, mg/l of Pt in the chloroplatinate standard	
True	14
Apparent	28
Turbidity, mg/l of natural Si	23
pH	7.2

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[a] Shawnee Steam Plant is located near Paducah, Kentucky.

TABLE 22. INORGANIC SPECIES CONCENTRATIONS OF SETTLED MATERIALS SAMPLED OCTOBER 22, 1980, FROM RAW SHAWNEE STEAM PLANT SAMPLE COMPOSED OF 100 % (v/v) UNCHLORINATED UNIT NUMBER 5 CONDENSER DISCHARGE OUTLET WATER, COLLECTED OCTOBER 21, 1980[a,b]

Characteristics	Value
Inorganics, μg/l	
Arsenic	6
Chromium	< 1
Copper	30
Iron	8000
Mercury	<0.2
Manganese	650
Zinc	60

---

[a] Shawnee Steam Plant is located near Paducah, Kentucky.

[b] After the insoluble materials in the sample shown in Table 21 settled and aliquots of the supernatant were withdrawn for diluting chlorinated samples, the settled materials had been concentrated to yield a water slurry with the given characteristics.

TABLE 23. EXPERIMENTAL RECOVERY BY MC AND AT METHODS OF TOTAL CHLORINE FROM UNSPIKED, CHLORINATED SHAWNEE STEAM PLANT CONDENSER COOLING RIVER WATER SAMPLES AND ONES SPIKED WITH CALCIUM HYPOCHLORITE[a]

Replicate Number	Total Chlorine (μg/1) MC	Total Chlorine (μg/1) AT	Mean MC	Mean AT	SD MC	SD AT	RSD (%) MC	RSD (%) AT	Total Chlorine Spike (μg/1) MC	Total Chlorine Spike (μg/1) AT
Experiment 23.1 Unspiked Sample Composed of 100 % (v/v) Unchlorinated Unit Number 5 Condenser Discharge Outlet Water Collected October 21, 1980, and Analyzed October 22, 1980[b]										
1	-2.0	<20	0.0200		1.24		6200			
2	0.3	<20								
3	0.2	<20								
4	1.4	<20								
5	0.2	<20								
6	32.3[c]	<20[c]								
7	37.7[c]	<20[c]								
Experiment 23.2 Unspiked Sample Composed of 10 % (v/v) Chlorinated Unit Number 4 Condenser Discharge Outlet Water and 90 % (v/v) Unchlorinated Unit Number 5 Condenser Discharge Outlet Water Collected October 21, 1980, and Analyzed October 22, 1980[b]										
1	5.2	<20	7.91		4.50		56.9			
2	4.1	<20								
3	8.7	<20								
4	3.4	<20								
5	6.0	<20								
6	14.7	<20								
7	13.3	<20								
Experiment 23.3 Spiked Sample Shown in Experiment 23.2[d,e]										
1	11.0	35	11.4	27.1	1.57	12.2	13.8	45.0	25	50
2	12.7	35								
3	9.6	30								
4	13.8	30								
5	11.4	40								
6	9.5	<20								
7	11.9	<20								

continued

TABLE 23. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 23.4 Unspiked Sample Composed of 25 % (v/v) Chlorinated Unit Number 4 Condenser Discharge Outlet Water and 75 % (v/v) Unchlorinated Unit Number 5 Condenser Discharge Outlet Water Collected October 21, 1980, but Composited and Analyzed October 22, 1980										
1	21	20								
2	22	30								
3	20	40								
4	21	40	20.0	32.9	1.4	7.0	7.0	21.3		
5	18	35								
6	19	30								
7	19	35								
Experiment 23.5 Spiked Sample Shown in Experiment 23.4[d,e]										
1	40	30								
2	36	20								
3	33	25								
4	30	<20	33.1	21.4	4.0	8.5	12.1	39.7	50	100
5	34	25								
6	31	30								
7	28	<20								
Experiment 23.6 Unspiked Sample Composed of 50 % (v/v) Chlorinated Unit Number 4 Condenser Discharge Outlet Water and 50 % (v/v) Unchlorinated Unit Number 5 Condenser Discharge Outlet Water Collected October 21, 1980, but Composited and Analyzed October 22, 1980										
1	45	60								
2	44	40								
3	45	50								
4	45	40	46.6	47.9	2.8	8.1	6.0	16.9		
5	51	40								
6	46	50								
7	50	55								

continued

TABLE 23. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 23.7 Spiked Sample Shown in Experiment 23.6[d]										
1	66	40	69.7	47.1	7.3	9.5	10.5	20.2	99	100
2	56	40								
3	71	40								
4	78	60								
5	72	60								
6	69	40								
7	76	50								
Experiment 23.8 Unspiked Sample Composed of 100 % (v/v) Chlorinated Unit Number 4 Condenser Discharge Outlet Water Collected October 21, 1980, and Analyzed October 22, 1980										
1	114	100	118	109	6.4	10.7	5.4	9.8		
2	111	120								
3	123	120								
4	113	120								
5	118	100								
6	129	100								
7	121	100								
Experiment 23.9 Spiked Sample Shown in Experiment 23.8[d]										
1	80	70	91.4	80.0	10.8	8.2	11.8	10.2	99	100
2	92	90								
3	99	90								
4	91	80								
5	85	80								
6	111	80								
7	82	70								

continued

TABLE 23. CONTINUED

Experiment 23.10 Unspiked Sample Composed of 75 % (v/v) Chlorinated Unit Number 4 Condenser Discharge Outlet Water and 25 % (v/v) Unchlorinated Unit Number 5 Condenser Discharge Outlet Water Collected and Analyzed October 21, 1980

Replicate Number	Total Chlorine (µg/l) MC	Total Chlorine (µg/l) AT	Mean MC	Mean AT	SD MC	SD AT	RSD (%) MC	RSD (%) AT	Total Chlorine Spike (µg/l) MC	Total Chlorine Spike (µg/l) AT
1	171	150	155	136	14.0	12.7	9.0	9.3		
2	169	120								
3	154	140								
4	131	140								
5	161	120								
6	152	150								
7	145	130								

Experiment 23.11 Spiked Sample Shown in Experiment 23.10[d]

Replicate Number	Total Chlorine (µg/l) MC	Total Chlorine (µg/l) AT	Mean MC	Mean AT	SD MC	SD AT	RSD (%) MC	RSD (%) AT	Total Chlorine Spike (µg/l) MC	Total Chlorine Spike (µg/l) AT
1	224	245	239	216	16.3	14.6	6.8	6.8	296	299
2	246	215								
3	264	225								
4	247	205								
5	242	215								
6	238	205								
7	214	205								

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[a] The Shawnee Steam Plant is located near Paducah, Kentucky. MC and AT are microprocessor-controlled ion selective electrode and forward amperometric titration methods, respectively. SD is standard deviation and % RSD is standard deviation expressed as percentage of mean.

[b] An additional significant figure was retained for use in calculating a precise estimate of minimum detection limit by MC.

[c] These values were omitted in calculation of mean, SD, and % RSD by MC and were obtained on settled materials sampled October 22, 1980 (See Table 22 for concentrations of inorganic species).

[d] Total chlorine is value obtained after subtracting the mean background concentration of unspiked sample.

[e] For the AT, results less than 20 µg/l were included in the statistical calculations as 10 µg/l.

TABLE 24. CHLORINE DEMAND OF RAW ALLEN STEAM PLANT SAMPLE COMPOSED OF 100 % (v/v) UNCHLORINATED UNIT NUMBER 3 CONDENSER DISCHARGE WATER INLET COLLECTED OCTOBER 28, 1980[a]

Contact Time (Min)	Chlorine Concentration, mg/l		
	Added	Found	Demand[b]
1	0.2	0.2	0.0
1	0.6	0.6	0.0
1	1.0	1.0	0.0
1	3.0	2.4	0.6
1	5.0	3.6	1.4
5	0.2	0.2	0.0
5	0.6	0.6	0.0
5	1.0	1.0	0.0
5	3.0	1.8	1.2
5	5.0	2.6	2.4
10	0.2	0.2	0.0
10	0.6	0.6	0.0
10	1.0	1.0	0.0
10	3.0	1.6	1.4
10	5.0	2.3	2.7
15	0.2	0.2	0.0
15	0.6	0.6	0.0
15	1.0	1.0	0.0
15	3.0	1.4	1.6
15	5.0	2.2	2.8
30	0.2	0.2	0.0
30	0.6	0.6	0.0
30	1.0	1.0	0.0
30	3.0	1.0	2.0
30	5.0	2.0	3.0
60	0.2	0.2	0.0
60	0.6	0.56	0.04
60	1.0	0.96	0.04
60	3.0	1.0	2.0
60	5.0	1.5	3.5

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[a] The Allen Steam Plant is located near Memphis, Tennessee.

[b] Demand is difference between total chlorine added initially as NaOCl-Cl_2 and that found after elapsed contact time.

TABLE 25. INORGANIC SPECIES CONCENTRATIONS, SANITARY CHEMICAL CHARACTERISTICS, AND PHYSICAL PROPERTIES OF RAW ALLEN STEAM PLANT SAMPLE COMPOSED OF 100 % (v/v) UNCHLORINATED UNIT NUMBER 3 CONDENSER DISCHARGE INLET WATER, COLLECTED OCTOBER 28, 1980[a]

Characteristics	Value
Inorganics, µg/l	
Arsenic	3
Chromium	< 1
Copper	20
Iron	1600
Mercury	< 0.2
Manganese	670
Zinc	20
Solids, mg/l	
Suspended	30
Dissolved	30
Chemical oxygen demand, mg/l	24
Total organic carbon mg/l	4.4
Nitrogen, mg/l as N	
Organic	0.37
Nitrite plus nitrate	0.95
Ammonia	0.45
Alkalinity, mg/l as $CaCO_3$	
Total	14
Phenol	< 1
Color, mg/l of Pt in the chloroplatinate standard	
True	50
Apparent	74
Turbidity, mg/l of natural Si	19
pH	7.4

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[a] The Allen Steam Plant is located near Memphis, Tennessee.

TABLE 26. EXPERIMENTAL RECOVERY BY MC AND AT METHODS OF TOTAL CHLORINE FROM UNSPIKED, CHLORINATED ALLEN STEAM PLANT CONDENSER COOLING RIVER WATER SAMPLES AND ONES SPIKED WITH CALCIUM HYPOCHLORITE[a]

Replicate Number	Total Chlorine (µg/l) MC	Total Chlorine (µg/l) AT	Mean MC	Mean AT	SD MC	SD AT	RSD (%) MC	RSD (%) AT	Total Chlorine Spike (µg/l) MC	Total Chlorine Spike (µg/l) AT
Experiment 26.1 Unspiked Sample Composed of 100 % (v/v) Unchlorinated Unit Number 3 Condenser Discharge Inlet Water, Collected October 28, 1980, and Analyzed October 29, 1980[b]										
1	2.0	<20	-0.83		2.22		267			
2	2.4	<20								
3	-3.3	<20								
4	-2.6	<20								
5	-2.1	<20								
6	-1.3	<20								
7	-0.9	<20								
Experiment 26.2 Unspiked Sample Composed of 5 % (v/v) Chlorinated Unit Number 3 Condenser Discharge Inlet Water, and 95 % (v/v) Unchlorinated Unit Number 3 Condenser Discharge Inlet Water Collected October 28, 1980, but Composited and Analyzed October 29, 1980[c]										
1	28	<20	21.1	21.1	3.2	8.5	15.2	40.3		
2	20	30								
3	22	<20								
4	20	30								
5	19	25								
6	19	20								
7	20	25								
Experiment 26.3 Spiked Sample Shown in Experiment 26.2[c,d]										
1	16	<20	19.0	19.3	3.7	12.1	19.5	62.7	25	25
2	14	25								
3	22	35								
4	22	<20								
5	24	35								
6	18	<20								
7	17	<20								

continued

TABLE 26. CONTINUED

Replicate Number	Total Chlorine (µg/l) MC	Total Chlorine (µg/l) AT	Mean MC	Mean AT	SD MC	SD AT	RSD (%) MC	RSD (%) AT	Total Chlorine Spike (µg/l) MC	Total Chlorine Spike (µg/l) AT
Experiment 26.4 Unspiked Sample Composed of 10 % (v/v) Chlorinated Unit Number 3 Condenser Discharge Inlet Water and 90 % (v/v) Unchlorinated Unit Number 3 Condenser Discharge Inlet Water Collected October 28, 1980, but Composited and Analyzed October 29, 1980										
1	39	45	46.9	45.0	5.0	4.1	10.7	9.1		
2	52	45								
3	44	45								
4	43	50								
5	50	40								
6	48	40								
7	52	50								
Experiment 26.5 Spiked Sample Shown in Experiment 26.4[d]										
1	38	35	28.3	34.3	8.2	7.3	29.0	21.3	50	50
2	20	30								
3	39	20								
4	32	40								
5	27	35								
6	21	40								
7	21	40								
Experiment 26.6 Unspiked Sample Composed of 15 % (v/v) Chlorinated Unit Number 3 Condenser Discharge Inlet Water and 85 % (v/v) Unchlorinated Unit Number 3 Condenser Discharge Inlet Water Collected October 28, 1980, but Composited and Analyzed October 29, 1980										
1	80	85	76.6	75.0	12.7	10.8	16.6	14.4		
2	90	90								
3	82	75								
4	85	70								
5	80	60								
6	66	80								
7	53	65								

continued

TABLE 26. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 26.7 Spiked Sample Shown in Experiment 26.6[c,d]										
1	38	20	41.1	25.7	2.5	9.3	6.1	36.2	50	50
2	44	30								
3	42	30								
4	40	20								
5	43	35								
6	43	35								
7	38	<20								
Experiment 26.8 Unspiked Sample Composed of 15 % (v/v) Chlorinated Unit Number 3 Condenser Discharge Inlet Water Collected October 28, 1980, and 85 % (v/v) of Mixture Shown in Experiment 26.2, but Composited and Analyzed October 29, 1980										
1	143	145	150	145	4.7	6.5	3.1	4.5		
2	155	155								
3	152	135								
4	145	140								
5	155	150								
6	149	145								
7	151	145								
Experiment 26.9 Spiked Sample Shown in Experiment 26.8[d]										
1	122	125	120	114	9.6	11.0	8.0	9.6	148	150
2	134	105								
3	123	125								
4	104	115								
5	126	105								
6	118	125								
7	113	100								

continued

TABLE 26. CONTINUED

Replicate Number	Total Chlorine (μg/1) MC	Total Chlorine (μg/1) AT	Mean MC	Mean AT	SD MC	SD AT	RSD (%) MC	RSD (%) AT	Total Chlorine Spike (μg/1) MC	Total Chlorine Spike (μg/1) AT
Experiment 26.10 Unspiked Sample Composed of 25 % (v/v) Chlorinated Unit Number 3 Condenser Discharge Inlet Water and 75 % (v/v) Unchlorinated Unit Number 3 Condenser Discharge Inlet Water Collected and Analyzed October 28, 1980										
1	250	160	247	177	7.0	15.8	2.8	8.9		
2	249	205								
3	256	170								
4	241	180								
5	250	190								
6	250	165								
7	235	170								
Experiment 26.11 Effect of 2 % (v/v) Sodium Pyrophosphate Decahydrate in Overcoming Chemical Interference for Total Chlorine Determinations on Sample Shown in Experiment 26.10										
1	168	140	163	148	5.0	10.4	3.1	7.0		
2	162	160								
3	158	145								
4										
5										
6										
7										
Experiment 26.12 Spiked Sample Shown in Experiment 26.10[d]										
1	180	165	157	132	12.3	24.3	7.8	18.4	245	199
2	156	155								
3	148	105								
4	154	105								
5	163	115								
6	141	135								
7	156	145								

continued

TABLE 26. CONTINUED

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[a] The Allen Steam Plant is located near Memphis, Tennessee. MC and AT are microprocessor-controlled ion selective electrode and forward amperometric titration methods, respectively. SD is standard deviation, and % RSD is standard deviation expressed as percentage of mean.

[b] An additional significant figure was retained for use in calculating a precise estimate of minimum detection limit by MC.

[c] For the AT, results less than 20 μg/l were included in the statistical calculation as 10 μg/l.

[d] Total chlorine is value obtained after subtracting the mean background concentration of unspiked sample.

TABLE 27. CHLORINE DEMAND OF RAW JOHN SEVIER STEAM PLANT SAMPLE COMPOSED OF 100 % (v/v) UNCHLORINATED UNIT NUMBER 1 CONDENSER DISCHARGE INLET WATER COLLECTED, NOVEMBER 4, 1980[a]

Contact Time (Min)	Chlorine Concentration, mg/l		
	Added	Found	Demand[b]
1	0.2	0.20	0.0
1	0.6	0.56	0.04
1	1.0	0.88	0.12
1	3.0	2.4	0.6
1	5.0	4.7	0.3
5	0.2	0.18	0.02
5	0.6	0.46	0.14
5	1.0	0.78	0.22
5	3.0	2.40	0.6
5	5.0	4.50	0.5
10	0.2	0.16	0.04
10	0.6	0.44	0.16
10	1.0	0.72	0.28
10	3.0	2.30	0.7
10	5.0	4.40	0.6
15	0.2	0.12	0.08
15	0.6	0.38	0.22
15	1.0	0.60	0.4
15	3.0	2.25	0.75
15	5.0	4.40	0.6
30	0.2	0.10	0.1
30	0.6	0.28	0.32
30	1.0	0.44	0.56
30	3.0	2.0	1.0
30	5.0	4.2	0.8
60	0.2	0.08	0.12
60	0.6	0.22	0.38
60	1.0	0.32	0.68
60	3.0	1.8	1.2
60	5.0	4.0	1.0

---

[a] The John Sevier Steam Plant is located near Rogersville, Tennessee.

[b] Demand is the difference between total chlorine added initially as $NaOCl-Cl_2$ and that found after elapsed time.

TABLE 28. CONCENTRATIONS OF INORGANIC SPECIES, SANITARY CHEMICAL CHARACTERISTICS, AND PHYSICAL PROPERTIES OF RAW JOHN SEVIER STEAM PLANT SAMPLE COMPOSED OF 100 % (v/v) UNCHLORINATED UNIT NUMBER 1 CONDENSER DISCHARGE INLET WATER COLLECTED NOVEMBER 4, 1980

Characteristics	Value
Inorganics, μg/l	
Arsenic	< 2
Chromium	< 1
Copper	< 10
Iron	380
Mercury	0.3
Manganese	50
Zinc	< 10
Solids, mg/l	
Suspended	7
Dissolved	150
Chemical oxygen demand, mg/l	8
Total organic carbon mg/l	2.5
Nitrogen, mg/l as N	
Organic	0.22
Nitrite plus nitrate	0.85
Ammonia	0.06
Alkalinity, mg/l as $CaCO_3$	
Total	72
Phenol	0
Color, mg/l of Pt in the chloroplatinate standard	
True	15
Apparent	21
Turbidity, mg/l of natural Si	43
pH	6.6

---

[a] The John Sevier Steam Plant is located near Rogersville, Tennessee.

TABLE 29. EXPERIMENTAL RECOVERY BY MC AND AT METHODS OF TOTAL CHLORINE FROM UNSPIKED, CHLORINATED JOHN SEVIER STEAM PLANT CONDENSER COOLING RIVER WATER SAMPLES AND ONES SPIKED WITH CALCIUM HYPOCHLORITE[a]

Replicate Number	Total Chlorine (μg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (μg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 29.1 Unspiked Sample Composed of 100 % (v/v) Unchlorinated Unit Number 1 Condenser Discharge Inlet Water Collected and Analyzed November 4, 1980[b]										
1	2.3	<20	2.10		0.40		19.0			
2	2.2	<20								
2	2.3	<20								
4	2.3	<20								
5	2.3	<20								
6	1.2	<20								
7	2.1	<20								
Experiment 29.2 Unspiked Sample Composed of 10 % (v/v) Chlorinated Unit Number 1 Condenser Discharge Inlet Water and 90 % (v/v) Unchlorinated Unit Number 1 Condenser Discharge Inlet Water Collected November 4, 1980, but Composited and Analyzed November 5, 1980[b,c]										
1	9.7	25	9.14	13.5	0.60	6.3	6.6	46.7		
2	9.1	<20								
3	8.8	<20								
4	10.1	<20								
5	8.3	<20								
6	9.2	<20								
7	8.8	20								
Experiment 29.3 Spiked Sample Shown in Experiment 29.2[b,c,d]										
1	4.5	<20	5.11	19.3	1.03	11.0	20.2	57.0	10	15
2	4.5	40								
3	4.7	<20								
4	4.2	20								
5	7.2	<20								
6	5.6	20								
7	5.1	25								

continued

TABLE 29. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 29.4 Unspiked Sample Composed of 25 % (v/v) Chlorinated Unit Number 1 Condenser Discharge Inlet Water and 75 % (v/v) Unchlorinated Unit Number 1 Condenser Discharge Inlet Water Collected November 4, 1980, but Composited and Analyzed November 5, 1980										
1	29	35	25.9	30.7	4.0	6.1	15.4	19.9		
2	25	40								
3	23	30								
4	26	35								
5	24	25								
6	33	25								
7	21	25								
Experiment 29.5 Spiked Sample Shown in Experiment 29.4[d]										
1	16	10	15.3	21.4	0.8	7.5	5.2	35.0	25	25
2	16	15								
3	14	20								
4	15	30								
5	16	20								
6	15	30								
7	15	25								
Experiment 29.6 Unspiked Sample Composed of 50 % (v/v) Chlorinated Unit Number 1 Condenser Discharge Inlet Water and 50 % (v/v) Unchlorinated Unit Number 1 Condenser Discharge Inlet Water Collected November 4, 1980, but Composited and Analyzed November 5, 1980										
1	55	50	55.3	57.9	3.0	7.6	5.4	13.1		
2	52	60								
3	57	50								
4	53	65								
5	61	65								
6	55	50								
7	54	65								

continued

TABLE 29. CONTINUED

Replicate Number	Total Chlorine (μg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (μg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 29.7 Spiked Sample Shown in Experiment 29.6[d]										
1	44	35	41.1	37.1	4.1	9.5	10.0	25.6	50	50
2	45	20								
3	44	35								
4	40	50								
5	33	40								
6	42	35								
7	40	45								
Experiment 29.8 Unspiked Sample Composed of 75 % (v/v) Chlorinated Unit Number 1 Condenser Discharge Inlet Water and 25 % (v/v) Unchlorinated Unit Number 1 Condenser Discharge Inlet Water, Collected November 4, 1980, but Composited and Analyzed November 5, 1980										
1	95	110	95.7	99.3	6.0	7.9	6.3	8.0		
2	93	100								
3	105	100								
4	103	85								
5	90	105								
6	90	100								
7	94	95								
Experiment 29.9 Spiked Sample Shown in Experiment 29.8[d]										
1	62	80	74.3	73.6	8.2	10.3	11.0	14.0	99	100
2	85	80								
3	73	80								
4	83	60								
5	69	70								
6	70	85								
7	78	60								

continued

EXPERIMENT 29. CONTINUED

Replicate Number	Total Chlorine (µg/l)		Mean		SD		RSD (%)		Total Chlorine Spike (µg/l)	
	MC	AT	MC	AT	MC	AT	MC	AT	MC	AT
Experiment 29.10 Unspiked Sample Composed of 100 % (v/v) Chlorinated Unit Number 1 Condenser Discharge Inlet Water Collected November 4, 1980, and Analyzed November 5, 1980										
1	137	130	139	131	3.9	8.4	2.8	6.4		
2	145	125								
3	139	135								
4	137	135								
5	137	135								
6	143	115								
7	134	140								
Experiment 29.11 Spiked Sample Shown in Experiment 29.10[d]										
1	132	125	131	119	3.3	8.4	2.5	7.1	148	150
2	132	115								
3	130	135								
4	125	120								
5	134	110								
6	135	115								
7	130	115								
Experiment 29.12 Unspiked Sample Composed of 100 % (v/v) Chlorinated Unit Number 1 Condenser Discharge Inlet Water Collected and Analyzed November 4, 1980										
1	294	230	316	252	15.0	13.5	4.7	5.4		
2	313	270								
3	326	250								
4	301	255								
5	338	260								
6	316	260								
7	323	240								

continued

TABLE 29. CONTINUED

Replicate Number	Total Chlorine (µg/l) MC	Total Chlorine (µg/l) AT	Mean MC	Mean AT	SD MC	SD AT	RSD (%) MC	RSD (%) AT	Total Chlorine Spike (µg/l) MC	Total Chlorine Spike (µg/l) AT
Experiment 29.13 Spiked Sample Shown in Experiment 29.12[d]										
1	215	245	194	226	14.2	11.8	7.3	5.2	245	249
2	188	235								
3	171	220								
4	205	215								
5	187	215								
6	200	235								
7	195	220								

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[a] The John Sevier Steam Plant is located near Rogersville, Tennessee. MC and AT are microprocessor-controlled ion selective electrode and forward amperometric titration methods, respectively. SD is standard deviation, and % RSD is standard deviation expressed as percentage of mean.

[b] An additional significant figure was retained for use in calculating a precise estimate of minimum detection limit by MC.

[c] For the AT, results less than 20 µg/l were included in the statistical calculations as 10 µg/l.

[d] Total chlorine is value obtained after subtracting the mean background concentration of unspiked sample.

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15. SUPPLEMENTARY NOTES

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16. ABSTRACT

A microprocessor-controlled ion selective electrode (MC) method was evaluated and compared to the forward amperometric titration (AT) method for determining total chlorine in condenser cooling river water from coal-burning electric plants. The effective range for quantification by the MC method is from the minimum detection limit of 6.5 μg/l chlorine for unspiked condenser water and 13.3 μg/l chlorine for spiked condenser water to 100 μg/l chlorine. Interferences by zinc(II), copper(II), iron(III), arsenic(III), and manganese(VII) are discussed. The pH, chromium(VI), mercury(II), bromide, and arsenic(V) do not interfere with measurement of total chlorine. For both unspiked and spiked condenser water, the overall pooled standard deviation and overall mean percentage relative standard deviation over concentrations of 20-200 μg/l chlorine are lower for the MC method than for the AT method. Standard deviations are discussed for the MC method over concentrations of 2-20 μg/l chlorine.

17. KEY WORDS AND DOCUMENT ANALYSIS

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